Subsurface Contamination

A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water by Deep Oxidation

Project ID: 54122

Ayusman Sen, The Pennsylvania State University

Research Objective

Toxic organics in water and soil constitute an important environmental hazard. The objective of the research is the design of practical procedures for the removal of toxic organic pollutants by deep oxidation.

Research Progress

This report summarizes the work performed in the course of a three year project. In water, metallic palladium was found to catalyze the deep oxidation of a wide variety of functional organics by dioxygen at 80-90°C in the presence of carbon monoxide or dihydrogen.[1-3] Several classes of organic compounds were examined: benzene, phenol and substituted phenols, nitro and halo organics, organophosphorus, and organosulfur compounds. In every case, deep oxidation to carbon monoxide, carbon dioxide, and water occurred in high yields, resulting in up to several hundred turnovers over a 24 h period. For substrates susceptible to hydrogenation, the conversions were generally higher with dihydrogen than with carbon monoxide. For organophosphorus compounds, the system presents the first examples of catalytic cleavage of phosphorous-alkyl bonds.

It is clear from the results obtained that we have discovered an exceptionally versatile catalytic system for the deep oxidation of toxic organics in water. This system possesses several attractive features not found simultaneously in other reported systems. These are (a) the ability to directly utilize dioxygen as the oxidant, (b) the ability to carry out the deep oxidation of a particularly wide range of functional organics, and (c) the ease of recovery of the catalyst by simple filtration. While our understanding of the mechanistic steps involved in the oxidation is far from complete, preliminary studies indicate that the overall transformation encompasses three catalytic steps in tandem. The first is the water-gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. The second catalytic step involves the combination of dihydrogen with dioxygen to yield hydrogen peroxide (or its equivalent). The third step in the oxidation process involves the metal catalyzed oxidation of the substrate by the hydrogen peroxide equivalent.

Finally, we have achieved the oxidative degradation and chemical recycling of a wide range of polymeric materials under relatively mild conditions using nitrogen oxides and dioxygen.[4] With the production of polymeric materials on the rise and landfill space at a premium, it becomes increasingly important to develop new techniques for reducing the amount of material lost to the landfill. While some condensation polymers are chemically recycled, there is very little, if any, recycling of addition polymers which constitute 75% by weight of all polymers manufactured. Using our procedure, a wide variety of addition and condensation polymers can be oxidatively degraded. In the particular cases of polystyrene, high and low density polyethylene and, perhaps, polypropylene useful organics are produced in moderate to good yields.

Publications

1. "A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water by Deep Oxidation Using Dioxygen as the Oxidant," Terrence Hogan, Robert Simpson, Minren Lin, and Ayusman Sen, *Catal. Lett.,* **1996**, 40, 95.
2. "The Deep Oxidation of Chemical Warfare Agent Models: Facile Catalytic Oxidative Cleavage of Phosphorus-Carbon and Sulfur-Carbon Bonds using Dioxygen," Terrence Hogan, Robert Simpson, Minren Lin, and Ayusman Sen, *Catal. Lett.,* **1997**, 49, 59.

3. "A Broad Spectrum Catalytic System for the Deep Oxidation of Toxic Organics in Aqueous Medium Using Dioxygen as the Oxidant," Anne Pifer, Terrence Hogan, Benjamin Snedeker, Robert Simpson, Minren Lin, Chengyu Shen, and Ayusman Sen, *J. Am. Chem. Soc.*, **1999**, *121*, 7485.
4. "Chemical Recycling of Plastics to Useful Organics by Oxidative Degradation," Anne Pifer and Ayusman Sen, *Angew. Chem., Int. Ed.*, **1998**, *37*, 3306.

Electrochemical Processes for In-Situ Treatment of Contaminated Soils

Project ID: 54661

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Research Objective

The electro-osmotic (EO) flow rate is one of the major factors controlling influence the process performance. Many soil and solution parameters can affect the EO water transport. A number of theories about the EO flow in a capillary have been developed. However, there is no simple and acceptable correlation between the EO water transport and fundamental soil-water parameters, such as the soil water content, the soil surface charge density, and the electrolyte concentration. Consequently, we have tried to develop a semi-empirical equation, as a means to estimate the electro-osmotic water transport in the unsaturated soil. It is expected that the equation can provide a better foundation for the development of an in-situ remediation process for application to the vadose zone.

Research Progress and Implications

Electro-osmotic flow experiments were conducted under several conditions, namely, the solution pH, the electric field strength, the soil water content, and the electrolyte concentration. Results indicate that the EO flow is proportional to the extent of surface charge density and the intensity of electric field. This can be attributed to the negative charges on the soil surface. When an electric field is imposed to the soil-water system, the electrostatic force is the only driving force for the electro-osmotic flow. According to the Coulomb's law, the electrostatic force is a linear function of the intensity of electric field and the quantity of electric charges. Therefore, the EO flow is closely related to both the extent of surface charge density and the intensity of electric field.

The electrolyte concentration has no significant effect on the EO flow if the electrolyte ions do not interact with the soil (i.e., indifferent ions). The electrolyte concentration can only influence the zeta potential rather than the surface charge when there is no chemical reaction between the electrolyte and the soil. In other words, the electrolyte concentration effect compresses the thickness of the double layer but not change the surface charge density of the soil. Consequently, the electrolyte concentration effect is independent of the EO flow rate because the water flow is related to the surface charge density rather than the zeta potential.

The parabolic relationship between the EO flow and the water content was observed in this study. We used the infinite plate model to derive the correlation between the flow rate and the moisture of the soil. The basic assumption of the infinite model is that the shear stress at any surface element in the water layer is proportional to the rate of change of velocity across the element (i.e., the Newtonian fluid). The EO flow rate is theoretically proportional to the square of the soil water content.

The following equation was developed: $Q = K\sigma_0(dE/dx)\omega^2$. Where Q, K, σ_0, dE/dx, and ω, are electro-osmotic flow rate, characterized coefficient, surface charge density, potential gradient, and soil water content, respectively. The characterized coefficient, K, is a collection of several physical properties of the soil including the total soil mass (M), the specific surface area (Σ), and the pore size (w) of the soil and fluid viscosity (η), that is $K = kwM^2/\eta\Sigma^2$.

Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste

Project ID: 54926

Yoram Cohen, University of California

Executive Summary

There is a growing need in the areas of hazardous waste treatment, remediation and pollution prevention for new processes capable of selectively separating and removing target organic species from aqueous steams. Membrane separation processes are especially suited for solute removal from dilute solutions. They have the additional advantage of requiring less energy relative to conventional separation technologies (e.g., distillation, extraction and even adsorption processes). The major difficulty with current membranes is the poor longevity of polymeric membranes under harsh conditions (high temperature, harsh solvents and pH conditions) and the lack of selectivity of ceramic membranes. In our previous work (1996 EMSP project), a first generation of novel polymer-ceramic (PolyCer) composite membranes were developed with the goal of overcoming the above difficulties. The proposed PolyCer membranes are fabricated by a surface-graft polymerization process resulting in a molecular layer of polymer chains which are terminally and covalently anchored to the porous membrane support. The polymer imparts the desired membrane selectivity while the ceramic support provides structural integrity. The PolyCer membrane retain its structural integrity and performance even when the polymer phase is exposed to harsh solvent conditions since the polymer chains are covalently bonded to the ceramic support surface. To date, prototype PolyCer membranes were developed for two different membrane separation processes: (a) pervaporation removal of organics from aqueous systems; and (b) ultrafiltration of oil-in-water emulsions. Pervaporation PolyCer membranes were demonstrated for removal of selected organics (TCE, chloroform and MTBE) from water with permeate enrichment factors as high as 300. While the above results have been extremely encouraging, higher enrichment factors (>1000) should be sought for field applications. The above improvement is feasible by increasing the length and surface density of the grafted polymer chains. The required simultaneous increase in surface polymer graft density and chain length is beyond the capability of present free-radical graft polymerization methods. Therefore, it is proposed to develop a new approach to synthesizing the grafted polymer membrane phase via "living" free-radical polymerization. This approach should allow controlled growth of the grafted polymer chains while maintaining the advantage of high surface chain density possible with conventional free-radical polymerization. Optimization of the membrane surface layer will be sought by developing fundamental correlation between surface characteristics (e.g., topology, chain length and surface density) and membrane performance. The ability to tailor-design the grafted polymer surface with long polymer chains of a desired surface density is also advantageous in fabricating non-fouling ultrafiltration membranes for colloidal filtration.

Using the same "living" free-radical polymerization technology, as for the pervaporation membranes, ultrafiltration ceramic membranes with terminally anchored surface chains, can be produced to repel colloidal species, thus reducing membrane fouling while increasing permeate rejection. As an outcome of the 1996 EEMSP project, it was discovered that, with sufficiently long surface chains, significant increase in PolyCer UF membrane rejection is possible, especially at high tangential velocities. The fabrication, via "living" free-radical polymerization, and optimization of such non-fouling UF membranes is another goal of the proposed research. It is expected that this project will results in the demonstration of a commercially viable technology for the "tailor design" and optimization of a new class of selective and robust polymer-ceramic (PolyCer) membranes for aqueous waste treatment and water decontamination applications. The proposed PolyCer approach

will allow the rapid deployment of “field-ready” and task-specific membranes for recovery and recycle for remediation and pollution prevention applications.

Ion Transporting Pumps in Plant Cells

Project ID: 55097

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Research Objective

The long-term goal of this research is to learn how to engineer a plant to selectively extract metal cations such as the RCRA metals or radionuclides from the soil. The approach being pursued is based on first understanding how plants use membrane transporters (pumps) to take up metals from the soil. The specific focus is on a family of heavy metal pumps that use ATP to drive the high affinity transport of ions across membranes. Heavy metal pumps are known to transport metals such as manganese, copper, molybdenum, zinc, cadmium and silver. The objective is to understand how these pumps selectively transport various metals. With that knowledge, it is expected that new transport systems can be designed that will increase the efficiency of plants to take up various toxic elements, such as plutonium. Modified transport systems will be introduced into plants by genetic engineering.

Research Progress and Implications

Three metal ion pumps are being studied in a model plant system *Arabidopsis*. One pump (AMA1) is a member of a subfamily of heavy metal pumps. Genetic evidence indicates that AMA1 is involved in molybdenum uptake, as indicated by a deficiency of this micronutrient in a plant line harboring a disruption of the AMA1 gene. This nutrient deficiency is reversed in mutant plants that have been transformed with an AMA1 pump under the control of a constitutive promoter (35s). Two other pumps being studied (ECA1 and ACA2) are members of two different subfamilies of calcium pumps. Genetic evidence suggests that (i) both pumps can also transport cerium (which has chemical properties similar to plutonium), and (ii) ECA1, but not ACA2, can also transport manganese, as indicated by the ability of these pumps to provide yeast with an increased resistance to toxic levels of these metals. These molybdenum and calcium pumps may be useful in engineering plants with an increased capacity to uptake and accumulate toxic metals.

Molecular Dissection of the Cellular Mechanisms Involved in Nickel Hyperaccumulation in Plants

Project ID: 54898

Dr. David E. Salt, Northern Arizona University

Research Objectives

Phytoremediation, the use of plants for environmental cleanup of pollutants, including toxic metals, holds the potential to allow the economic restoration of heavy metal and radionuclide contaminated sites. A number of terrestrial plants are known to naturally accumulate high levels of metals in their shoots (1-2 % dry weight), and these plants have been termed metal-hyperaccumulators. Clearly, the genetic traits that determines metal-hyperaccumulation offers the potential for the development of practical phytoremediation processes. Our long-term objective is to rationally design and generate plants ideally suited for phytoremediation using this unique genetic material.

Initially, our strategy will focus on isolating and characterizing the key genetic information needed for expression of the metal-hyperaccumulation phenotype. Recently, histidine has been shown to play a major role in Ni hyperaccumulation. Based on this information we propose to investigate, at the molecular level, the role of histidine biosynthesis in Ni hyperaccumulation in *Thlaspi goesingense*, a Ni hyperaccumulator species.

- We will clone key genes involved in histidine biosynthesis. ✓
- We will characterize their transcriptional and post transcriptional regulation by histidine, Ni. ✓
- We will determine if any of these genes are essential and sufficient for Ni hyperaccumulation by their expression in the non-hyperaccumulator *Arabidopsis thaliana*.

Research Progress and Implications

Cloning the Genes in Involved in histidine Biosynthesis in *T. goesingense*

In our last progress report (1997 – 1998) we outlined how we had successfully cloned and characterized *THG1*, *THD1* and *THB1*, encoding for the enzymes ATP phosphoribosyltransferase (ATP PRT), imidazoleglycerol phosphate dehydratase (IGPD), and histidinol dehydrogenase (HD), respectively. We have now used these cloned genes to investigate the role of histidine in Ni hyperaccumulation in *T. goesingense.*

Regulation of Hisitidine Biosynthesis by Nickel in *T. goesingense*

In *E. coli* ATP PRT is an important control point for histidine biosynthesis, being regulated at the level of transcription, translation and allosteric activation/inhibition. The highly regulated nature of ATP PRT in *E. coli* suggests that it might also play a key regulatory role in plants, making it a likely target for regulation of histidine biosynthesis by Ni. However, Northern analysis of the *THG1* RNA message clearly demonstrated that Ni does not induce or suppress transcription of the *THG1* mRNA in either the roots or shoots of *T. goesingense* (Fig 1). Because it is possible that ATP PRT is not the key regulated step in histidine biosynthesis in plants we also analyzed expression of two other genes in the histidine biosynthetic pathway, *THB1* and *THD1*, which encode the enzymes IGPD and HDH respectively. The IGPD enzyme catalyzes the conversion of imidazolglycerol phosphate to imidazoleacetol phosphate, the first step after the branch point, which feeds into the purine recycling pathway. This enzyme also catalyzes the conversion of L-histidinol phosphate to L-histidinol. Because of its key position in the histidine biosynthetic pathway this enzyme may also be regulated. Histidinol

dehydrogenase (HDH) catalyzes the oxidation of L-histidinol to L-hisitidine, the final step in histidine biosynthesis. Because this catalytic step uses NAD^+ as an oxidant it is possible that it is also regulated.

Northern analysis of the mRNA levels for both *THB1* and *THD1* clearly showed that expression of these mRNAs is not induced or repressed by Ni treatment in either the roots or the shoots of *T. goesingense* (Fig 1). Because *THG1*, *THB1* and *THD1* mRNA expression levels are not changed by Ni treatment, it is unlikely that control of the histidine biosynthetic pathway, at the transcriptional level, by Ni is involved in Ni hyperaccumulation in *T. goesingense*.

To determine if Ni modifies histidine biosynthesis at the post-translational level in *T. goesingense* we also analyzed the concentration of free histidine in root, xylem sap and shoot tissue. It is clear from this data (Table 1) that histidine concentrations remain basically unchanged after Ni exposure in both the xylem sap and the shoots. Interestingly, we did observe a large decrease in histidine concentrations in the root tissue after Ni exposure, however this was not reflected in the expression levels of *THG1*, *THB1* or *THD1* in the roots. At present we have no explanation for this loss of histidine, however it may reflect either increased catabolism or efflux of histidine in roots. However, recent analysis of *T. goesingense* root exudate showed no increases in rates of histidine exudation from roots after exposure to Ni (Salt et al., 1999a).

This biochemical data strongly supports the molecular evidence that free histidine concentrations in *T. goesingense* are not regulated by Ni exposure. It is possible, however, that the constitutive concentration of free histidine observed in *T. goesingense* is sufficient to fulfill its theorized role in Ni hyperaccumulation. To test this hypothesis we compared the histidine concentration in *T. goesingense* and the non-accumulator *T. arvense*. This comparison revealed that the non-accumulator *T. arvense* contained equal concentrations of histidine in both roots, shoots and xylem sap as that found in *T. goesingense* during Ni exposure. The histidine concentration in the xylem sap of *T. goesingense* after Ni exposure is also similar to that measured in other non-accumulators. This strongly supports the case that there are no significant differences in histidine metabolism between the accumulator and non-accumulator species of *Thlaspi*.

If free histidine is involved in the hyperaccumulation of Ni, as has been suggested occurs in *Alyssum* species, we would predict that histidine binds Ni within the plant. To directly address this hypothesis we used X-ray absorption spectroscopy (XAS) to determine the *in planta* coordination environment of the Ni in both the hyperaccumulator and non-accumulator *Thlaspi* species (Table 2). From this data it is clear that histidine or a histidine-like molecule is involved in coordinating Ni in both the roots and shoots of *T. goesingense* and *T. arvense*. However, the concentration of the Ni-histidine complex in the shoots of the non-accumulator *T. arvense* appears to be approximately 5-10 fold higher than in *T. goesingense*, and equal in the roots. Again, supporting the conclusion that free histidine does not play a key role in Ni hyperaccumulation in *T. goesingense.*

Future Directions

We are now in the process of overexpressing *THG1*, *THB1* and *THD1* in *A. thaliana*, to determine if any of these genes are essential and sufficient for Ni hyperaccumulation.

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Publications Supported by this Grant

Persans M, Yan X, Patnoe JMML, Krämer U, Salt DE (1999) Molecular dissection of histidine's role in nickel hyperaccumulation in *Thlaspi goesingense* (Hálácsy). Plant Physiol (submitted).

Salt DE (1999) Phytoextraction: Present Applications and Future Promise. In *Remediation of Hazardous Waste Contaminated Soils*, 2nd Edition, DL Wise, DJ Trantolo, HI Inyang, EJ Cichon (eds.), Marcel Dekker, Inc., (in press)

Salt DE and Krämer U (1999) Mechanisms of Metal Hyperaccumulation in Plants. In: *Phytoremediation of Toxic Metals: Using Plants to Clean-Up the Environment*, Burt D. Ensley and Ilya Raskin (eds.), Chapter 13, John Wiley & Sons, Inc., New York, NY, USA (in press).

Salt DE, Kato N, Krämer U, Smith RD and Raskin I (1999a) The role of root exudates in nickel hyperaccumulation and tolerance in accumulator and non-accumulator species of *Thlaspi*. In: *Phytoremediation of Contaminated Soil and Water*, Terry, N., Bañuelos, G.S. (eds.), Chapter 10, pp 191-202, CRC Press LLC, Boca Raton, FL, USA (in press).

Salt DE, Prince RC, Baker AJM, Raskin I, Pickering, IJ (1999b) Zinc ligands in the metal hyperaccumulator *Thlaspi caerulescens* as determined using X-ray absorption spectroscopy. Environ Sci Technol **33**: 713-717.

Persans M, Yan X, Smith R, Salt DE (1998) Cloning of two cDNA's from the Ni hyperaccumulator *Thlaspi goesingense*: Histidinol dehydrogenase (Accession No. AF023141) and imidazolglycerol-phosphate dehydratase (Accession No. AF023140), two enzymes in the histidine biosynthetic pathway. Plant Physiol Plant Gene Register **117**:332.

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Ann Rev Plant Physiol Plant Mol Biol **49**: 643-668.

Krämer U, Smith RD, Wenzel W, Raskin I, Salt DE (1997) The role of nickel transport and tolerance in nickel hyperaccumulation by *Thlaspi goesingense* Hálácsy. Plant Physiol **115**: 1641-1650.

Table 1. Free histidine content of *Thlaspi goesingense* tissues exposed to 50 µM Ni for 7 days

	SHOOT	ROOT	XYLEM SAP
	nmol g^{-1} fresh biomass		*µmol L^{-1}*
T. goesingense			
Control	136 ± 37 (4)	742 ± 188 (4)	7.4 ± 3 (4)
Nickel treated	107 ± 62 (5)	68 ± 30 (7)	18.2 ± 9 (6)
T. arvense			
Control	73 ± 16 (4)	43 ± 9 (3)	57 ± 31 (8)
Nickel treated	n.a.	n.a.	n.a.

Histidine was measured by HPLC as the phenylthiocarbamyl amino acid derivative with methionine sulfoxide as the internal standard. n.a.: not available.

Table 2. Nickel coordination by histidine ligands in *T. goesingense* and *T. arvense* measured by X-ray absorption spectroscopy (XAS)

	T. goesingense		*T. arvense*	
Time (d)	Shoot	Root	Shoot	Root
		mmol Kg^{-1} Dry Biomass		
1	0.2	2.5	0.4	2.9
3	0.1	2.5	1.0	3.9
5	0.4	2.6	1.2	4.3
7	0.2	4.1	1.3	6.1

Plants were exposed to 10 µM $Ni(NO_3)_2$ in the hydroponic solution. By fitting X-ray absorption spectra of aqueous Ni^{2+} and Ni^{2+} coordinated with histidine (6.66 mM $Ni(NO_3)_2$, 80 mM histidine, 30% glycerol, pH 7.0), citrate (6.66 mM $Ni(NO_3)_2$, 70 mM citrate, 30% glycerol, pH 8), glutamine (1 mM $Ni(NO_3)_2$, 4 mM glutamine, 30% glycerol, pH 7.3), and isolated *T. goesingense* shoot cell wall material, we were able to determine the contribution of histidine as a ligand of Ni^{2+}.

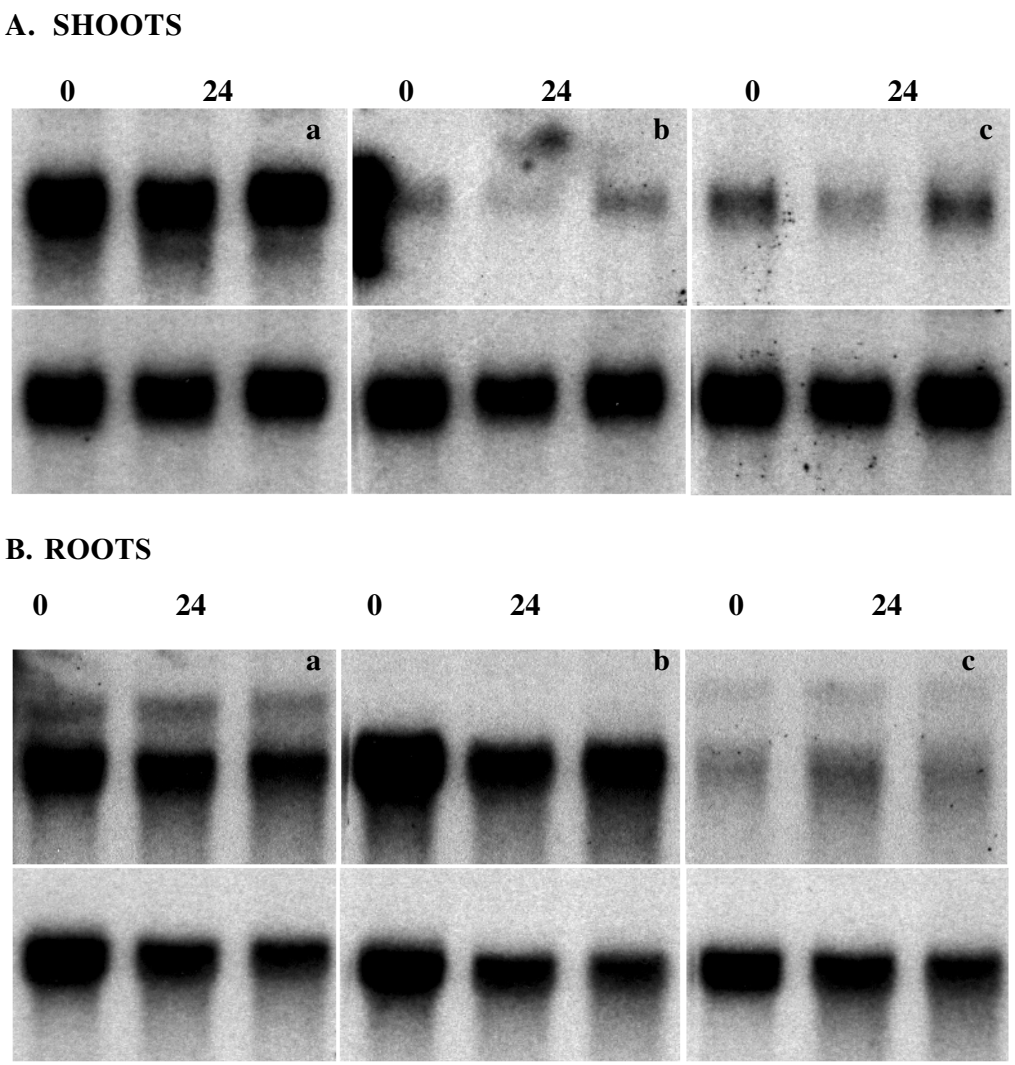


Figure 1. Northern blot analysis of the expression of *THG1*, *THD1*, and *THB1*. Total RNA was isolated from *T. goesingense* root and shoots tissue and probed with ^{32}P labeled *THG1*(a), *THB1*(b) and *THD1*(c) cDNA's probes (upper panel). Total RNA was also probed with an *A. thaliana* ^{32}P labeled actin cDNA fragment as a loading control (lower panel).

Molecular Characterization of a Novel Heavy Metal Uptake Transporter from Higher Plants & its Potential for use in Phytoremediation

Project ID: 55041

Dr. Julian I. Schroeder, University of California at San Diego

Research Progress

Soils with high levels of heavy metals such as Cd, Cr and Pb are detrimental to human and animal health. Many human disorders have been attributed to environmental contamination by heavy metals. Removal of heavy metals from highly contaminated soils is therefore a very costly but necessary process that is currently being pursued. Excavation and re-burial of top layer soils is the current, relatively inefficient, approach for decontamination of specific sites. Recent research indicates that uptake of heavy metals into plants via the root system may provide a cost effective approach for decontamination of heavy metal-laden soils. Several mechanisms have been identified which allow detoxification of heavy metals once they have reached the inside of plant cells, including binding to chelating substrates and transporting heavy metals into the plant cell vacuoles which function as storage organelles. However, the molecular biological mechanisms by which heavy metals are transported across the plasma membrane into root cells remain completely unknown. It has been suggested that passive uptake by ion channels, by heavy metal transporters, and by conjugated-metal transporters together could allow concentration of heavy metals by approximately 105-fold inside plant cells with respect to soil concentrations. However, no information has been obtained regarding the plant cDNAs that encode plasma membrane transporters which are able to catalyze the uptake of heavy metals.

By pursuing a genetic approach, we have cloned a cDNA from wheat roots, named PMT1, that shows a novel primary structure and contains several hydrophobic putative membrane-spanning domains. Expression of the PMT1 cDNA enhances the sensitivity of growth to Cd2+. Furthermore, PMT-expressing yeast cells show enhanced uptake of Cd, Pb and Ca2+. Isolation of the wheat root PMT1 cDNA will allow us to address questions regarding mechanisms of heavy metal uptake across the plasma membrane of plant cells and may contribute to testing future bioengineering of heavy metal removal by plants. We propose studies which will test the following hypotheses:

1. PMT1 functions as a plasma membrane heavy metal and Ca2+ uptake transporter isolated from higher plant roots.
2. Overexpression of the PMT1 cDNA in plants can be used to enhance plasma membrane heavy metal uptake into plant tissues.

To test these hypotheses we suggest experiments with the following specific aims:

I. Characterize the selectivity of PMT1 for uptake of toxic heavy metals such as Cd, Pb, Cr, Cu and nutrients such as Ca2+ and Mg2+. Competition among nutrient metals and heavy metals for uptake will further be studied.
II. Determine whether PMT1 itself represents a metal transporting membrane protein. The plasma membrane localization of the PMT1 protein will be analyzed and structural mutations in PMT1 which enhance heavy metal uptake will be isolated using a genetic selection system in yeast.
III. Low-stringency hybridizations will be used to determine whether PMT1 is a member of a larger gene family and RNA expression levels of PMT1s will be analyzed. PMT1 hybridization to mRNAs isolated from known heavy metal hyper accumulating plants will be pursued.

IV. PMT1 and PMT1 mutants that enhance heavy metal uptake will be overexpressed in transgenic plants to determine whether PMT1 expression can enhance heavy metal uptake. Transgenic PMT1 overexpressing plants will be quantitatively analyzed for growth phenotypes, and heavy metal and nutrient accumulation.

Molecular Genetics of Metal Detoxification: Prospects for Phytoremediation

Project ID: 55278

Dr. David W. Ow, United States Department of Agriculture

Research Objective

We seek to define the genes involved in heavy metal tolerance and sequestration. Initially, two complementary strategies were taken: 1) clone and characterize the genes that complement cadmium hypersensitive mutants of fission yeast, specifically those responsible for production of metal-binding complexes, and 2) isolate genes that can confer cadmium hypertolerance to wild type strains of fission yeast. During the course of the investigation, we added a third strategy to the existing plan. In this third strategy, we sought to isolate the cDNAs that are specifically expressed during exposure to Cd.

For the past year, the success in isolating a large number of genes using the second and third strategy has redirected our emphasis to concentrating on the characterization of these genes. Consequently, some of the work that was initiated with the first strategy has been put on hold.

Research Progress and Implications

Strategy #1: Mutant analysis (update from previous reports).

Mutant JS563: This work has been published (*J Biol Chem* 274:12350-13257, 1999). Cd sensitivity in this mutant was found to be due to a mutation in a gene encoding a mitochondrial sulfide:quinone oxidoreductase, which we have named HMT2. Its normal function appears to detoxify excess sulfide in the mitochondria resulting from metal-induced sulfide production. Interestingly, homologous enzymes may be widespread in higher organisms. Sulfide oxidizing activities have been described previously in animal mitochondria, and genes of unknown function, but with similarity *hmt2*$^+$, are present in the genomes of flies, worms, rats, mice and humans. This suggests a common tolerance mechanism in diverse higher organisms.

Mutant JS282: The analysis of a 7 kb genomic DNA that complements this mutant, which hypoproduces phytochelatins, led to an interesting 0.8 kb mRNA that is specifically induced by Cd, but not by other metals (Cu, Hg, Se, Zn) or agents that cause oxidative stress or heat stress. The expression of this gene is Cd concentration-dependent, with higher levels of mRNA accumulation corresponding to higher levels of Cd exposure. Removal of Cd from the media leads to rapid down-regulation of mRNA abundance. The promoter for this gene contains putative AP-1 binding motifs and the 3' untranslated region contains four AUUUA motifs that are important for mRNA degradation or stability. We assume that the AUUUA motifs are at least partially responsible for the rapid disappearance of the 0.8 kb transcript upon removal of Cd. The genetic signals that provide metal-specific transcript initiation and stability could be used for engineering of metal-responsive remediation genes.

Strategy #2. Genes that confer hypertolerance.

S. pombe cDNAs. A collection of cDNAs derived from *S. pombe* has been shown to confer high level Cd-tolerance when hyperexpressed in *S. pombe*. Upon further screening and sequencing, we have limited the analysis to 19 unique clones. These have been grouped into 6 classes: 1). Cd binding, 2) Signal transduction, 3) Biochemical pathway genes, 4) Stress related genes, 5) Ribosomal

genes, and 6) Unknown (novel) genes. A subset of the genes also confers tolerance to oxidative stress agents such as diamide and tbHOOH.

Brassica juncea cDNAs. 9 cDNAs from Indian Mustard, a metal-hyperaccumulating plant, can confer Cd-hypertolerance to *S. pombe*. To date, 5 have been sequenced, which revealed 4 unique genes, but two of the 4 are different members of the same gene family. Interesting, none shows extensive sequence similarity to genes outside of the plant kingdom. These suggest that they could encode functions that may be unique to plants. One cDNA appears to encode a metalloreductase-like protein.

Strategy #3. Genes expressed specifically during Cd-stress.

Substractive hybridization was used to isolate a collection of ~250 clones that are expressed during Cd stress. 50 of these have been sequenced. Since this screen was based on expression, but not on function, most of the cDNA clones are not full length. Based on the sequence of these partial genes, many of the deduced peptides appear to share similarity with proteins associated with oxidative stress, while a few have metal binding domains and may be involved in Cd binding. Of particular interest is a clone which encodes a product with sequence similarity to ABC transporters, the class of proteins in which a member has been shown to be involved in vacuolar sequestration of Cd.

Planned Activities

Due to the large number of genes isolated from *S. pombe* and *B. juncea* by the second strategy, most of the planned activities for the coming year will be devoted to the characterization of these genes. Since these cDNAs already exhibit a metal-hypertolerance function that would be useful for bioremediation, our highest priority is to test their activity in a plant. The planned experiments are: 1) For the 19 *S. pombe* cDNAs, we will engineer their expression in Arabidopsis. 2) For 9 *B. juncea* cDNAs, we will complete the DNA sequence for the remaining 4 clones. We will then engineer the expression of these cDNAs in Arabidopsis. The transgenic plants will be tested for tolerance and accumulation of Cd. For the *B. juncea* clone that shows sequence similarity to a metalloreductase, we will test biochemical activity.

From the third strategy clones, we will narrow our focus to a few promising candidates. Full length cDNAs from these selected candidates will be isolated and expressed in *S. pombe* and Arabidopsis to test for functional expression.

Information Access

1996 Ow, D.W. Heavy metal tolerance genes: prospective tools for bioremediation. *Resources, Conservation and Recycle* 18: 135-149.

1997 Perego, P., VandeWeghe, J., Ow, D.W., Howell, S.B. The role of determinants of cadmium sensitivity in the tolerance of *Schizosaccharomyces pombe* to cisplatin. *Molecular Pharmacology* 51: 12-18.

1998 Ow, D.W. Prospects of engineering heavy metal detoxification genes in plants. In: *Engineering crops for industrial uses* (Shewry, P., ed), Portland Press. pp. 111-124.

1999 VandeWeghe, J., Ow, D.W. A fission yeast gene for mitochondrial sulfide oxidation. *Journal of Biological Chemistry,* 274: 13250-13257.

1996 Zankel, T.C., Ow, D. Homologs of the human BTF3 and Wiskott-Aldrich syndrome proteins are involved in the metal stress response of *S. pombe*. Abstracts of the 1996 Keystone Symposium on Transcriptional Mechanisms, Taos, NM (March 17-23), page 67. (Abstract).

1996 Perego, P., VandeWeghe, J., Ow, D., Howell, S. B. Mechanisms of resistance to cisplatin (DDP) in *Schizosaccharomyces pombe*. (87th Annual Meeting of the American Association for Cancer Research, Washington, D.C., USA, April 20-24, 1996) Proceedings of the American Association for Cancer Research Annual Meeting, v.37, (1996): 336. (Abstract)

1996 VandeWeghe, J., Ow, D.W. An oxidoreductase-like gene required for cadmium tolerance in *Schizosaccharomyces pombe*. Abstracts of the 1996 Yeast Genetics & Molecular Biology Meeting, Univ of Wisconsin (August 6-11), p. 309 (Abstract)

1996 Ow, D. W. Prospects of engineering heavy metal detoxification genes in plants. Abstracts of the Symposium on Engineering Crops for Industrial End Uses. Bristol, England (Sept 16-18, 1996) (Abstract)

1997 Zankel, T.C., Ow, D.W. A *Schizosaccharomyces pombe* homolog of the Wiskott-Aldrich syndrome protein is involved in stress adaptation and mating. Abstracts of the 1997 Keystone Symposium on Temporal and Spatial Determinants of Specificity in Signal Transduction, Keystone, CO (March 31-April 6) (Abstract).

1997 VandeWeghe, J., Ow, D.W. A novel mitochrondrial oxidoreductase required for phytochelatin accumulation and cadmium tolerance in fission yeast. Abstracts of the Society for Experimental Biology Annual Meeting, Session on Metals and Genes, Canterbury, England. April 7-8, 1997, p. 80. (Abstract).

1997 Perego, P; Vandeweghe, J; Ow, D; Howell, S B. Role of determinants of cadmium sensitivity in the sensitivity of Schizosaccharomyces pombe to cisplatin. (Eighty-eighth Annual Meeting of the American Association for Cancer Research, San Diego, California, USA, Proceedings of the American Association for Cancer Research Annual Meeting, v.38, p. 393.

1997 Ow, D.W. VandeWeghe, J., Zankel, T., Henstrand, J., Clark, S., Kim, J. Heavy metal tolerance genes for phytoremediation. Abtracts of the 5th International Congress of Plant Molecular Biology, 9/21/97-9/27/97, Singapore.

1997 Ow, D.W. Heavy metal tolerance genes as tools for phytoremediation. Abstracts of the International Symposium on Environmental Engineering, 9/29/97-10/1/97, Kyongju, Korea.

1998 Ow, D.W., Clark, S., Henstrand, J., Kim, J. Molecular genetics of heavy metal tolerance. Abstracts of the University of Connecticut Agricultural Biotechnology Symposium, Storrs, CN, June 19-20, 1998. (Abstract)

1998 Ow, D.W., VandeWedge, J., Zankel, T., Clark, S., Henstrand, J., Kim, J. Heavy metal tolerance genes. Abstracts of the DOE Environmental Remediation Meeting, Chicago, IL, July 27-30, 1998. (Abstract)

Using Trees to Remediate Groundwaters Contaminated with Chlorinated Hydrocarbons

Project ID: 54889

Dr. Stuart E. Strand, University of Washington

Research Objective

Phytoremediation has emerged as a treatment alternative that combines the low cost of intrinsic remediation with the more active and adaptable characteristics of conventional remediation. Our lab has shown that fast-growing and deep-rooted hybrid poplar take up and transpire trichloroethylene (TCE) at a high rate, and that significant amounts of TCE are oxidized to carbon dioxide. These findings have been confirmed with axenic tissue cultures and with unique laboratory bioreactors that provide complete mass balance acounting of the fate of TCE carbon with whole plants. Ongoing field trials of small plots of poplar exposed to TCE have provided striking confirmation of the ability of these trees to completely prevent the movement of TCE through a barrier of densely planted poplar. We have also made significant progress in identifying the mechanism of TCE degradation in poplar (cytochrome P-450 IIE 1) and in constructing transgenic plants with enhanced capability for degradation of chlorinated hydrocarbons (CHCs). Finally recent evidence suggests that poplar will also be capable of uptake and oxidation of carbon tetrachloride.

We propose to test the ability of several plant clones to take up and transform various CHCs, including carbon tetrachloride, chloroform, dichloromethane, 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, the dichloroethylenes, and vinyl chloride using laboratory mass balance reactors. Screening methods have been developed that permit testing of plants from contaminated sites for those able to oxidize and sequester chlorinated compounds. In order to predict the best location and size of the plantation and hydrogeological models will be developed which include uptake of water and pollutants from the aquifer by trees. We will identify the mechanisms involved in CHC oxidation in poplar. We enhance that activity by amplifying expression of native monooxygenases or mammalian P-450s in poplar.

We anticipate that these approaches will provide powerful new tools for the remediation arsenal: selfmaintaining, solar-driven, pump-and-treat systems.

Background and Significance

Industrial practices in the past have resulted in contamination of groundwater with chlorinated hydrocarbons (CHCs) at many DOE sites, such as Hanford and Savannah River. Such contamination is a major problem because existing groundwater remediation technologies are expensive and difficult. An inexpensive method for groundwater remediation is greatly needed.

An alternative to costly conventional technologies is intrinsic remediation, which uses natural processes intrinsic to some polluted groundwaters that result in degradation, dilution or immobilization of the pollutant before adverse health effects can occur. Unfortunately not all sites have the requisite conditions to permit intrinsic remediation to occur at a rate which make it a viable option. Frequently, it is unclear whether there is sufficient electron donor present to maintain the requisite anaerobic conditions to sustain intrinsic remediation of CHCs for the time required to treat all of the pollutant that may be present. Furthermore, intrinsic remediation relies on natural groundwater flow to flush the polluted aquifer clean, extending the time required for cleanup.

Recently another option has emerged that combines the minimal intervention and costs of intrinsic remediation with the more active and adaptable characteristics of conventional remediation approaches. This option is phytoremediation and the University of Washington has taken a leading

role in its application to groundwaters polluted with CHCs. Phytoremediation is the use of plants to clean up contaminated soil, water and air.

Trees could be used to provide an active remediation zone and barrier to pollutant movement at minimal cost. Cost analysis suggests that phytoremediation would cost less than half the cost of conventional pump-and-strip technology over the 30-year life of the project. Since most of the cost of phytoremediation would be due to monitoring requirements, this outlay would be comparable to that required for intrinsic remediation. Poplar wood is valuable as a source of chips for paper making and its sale would partially offset the cost of phytoremediation. Poplar grow rapidly, reaching 30 m in nine years. Their roots seek out water from depths up to 20 m. Their transpiration rate is very high and their ability to prevent the movement of nitrate contaminated water off agricultural sites has been well demonstrated. Approximately 80% of the CHC polluted aquifers in the US are within 20 m of the surface, thus potentially accessible to poplar roots.

Poplar could be used to assist in the clean up of the contaminated groundwater at Hanford with beneficial effects on the major mobile pollutants: nitrate, carbon tetrachloride and tritium. A phytoremediation barrier could be established across the contaminated plume as it approaches the Columbia River. Near the river the plume is shallow enough for trees to access the groundwater. A sufficiently large plantation of densely planted poplar could prevent the plume from reaching the river. These trees would easily take up and assimilate the nitrate. Tritium contaminated water would be assimilated into plant tissue and transpired to the atmosphere, where sufficient dilution exists to prevent serious harm. Carbon tetrachloride would be transpired, metabolized and sequestered in plant tissue, and oxidized to carbon dioxide, depending on the trees planted. Over the lifetime of the plantation (50 years or more) trees would be harvested, sold for pulp, and new trees would be planted. A poplar plantation barrier would be much less expensive than other active remediation technologies.

Before phytoremediation can be extensively applied, we must determine the range of compounds that are attacked, the effects of metabolic products on the plants and the environment, and the effect of transpiration and concentration of CHC on uptake and metabolism. Aside from TCE very little is known of what other CHCs can be transported and/or oxidized by plants. A survey should be made of the CHC degradation ability of trees adapted to growth in various locales so that phytoremediation can be applied across the country. Little is known about the distribution of CHC degradation capability in plants. These capabilities should be surveyed by testing a wide variety of plants. Trees already growing on contaminated sites should be tested to determine if they have adapted by metabolizing the pollutants. Hydrogeological models that include the effects of trees on groundwaters polluted with CHCs are needed to provide rules for designing phytoremediation plantations. In order to capitalize on the promise of phytoremediation as illustrated by our findings of TCE metabolites in poplar tissue, we need to understand the mechanisms of plant metabolism of TCE and to explore transgenic mechanisms for increasing TCE degradation.

The Engineered Phytoremediation of Ionic and Methyl Mercury Pollution

Project ID: 70054

Dr. Richard B. Meagher, University of Georgia

Research Objective

Our long-term goal is to enable highly productive plant species to extract, resist, detoxify, and/or sequester toxic heavy metal pollutants (Meagher, 2000).

We have focused our research on the phytoremediation of soil and water-borne ionic and organic mercury (Meagher and Rugh, 1996; Meagher et al., 2000). Mercury pollution is a serious world-wide problem affecting the health of human and wild-life populations. The Department of Energy's Oak Ridge National Laboratory and Brookhaven National Laboratory have sites with significant levels of mercury contamination that could be cleaned by applying the scientific discoveries and new phytoremediation technologies described in this proposal. The experience gained engineering plants that hyperaccumulate mercury can be applied to extraction or accumulation of various heavy metal and radionucleide contaminates at dozens of DOE sites.

Research Progress and Implications

During the first grant period we successfully engineered several diverse plant species (e.g., *Arabidopsis,* tobacco, *Brassica napus*, yellow poplar, rice) to use a highly modified bacterial mercuric ion reductase gene, *merA*, to detoxify ionic mercury (Hg(II)), by reducing it to Hg(0) (Rugh et al., 1996; Heaton et al., 1998). MerA expressing tobacco and *Arabidopsis* seeds germinate and plants grow and set seed at normal growth rates on levels of Hg(II) that are lethal to normal plants. Pysiological experiments with transgenic yellow poplar and tobacco suggest these plants extract ionic mercury (Hg(II) from contaminated soil and water, reduce it to Hg(0), translocate Hg(0) up the vascular system, and transpire Hg(0) from leaves (Heaton et al., 1998; Rugh et al., 1998a; Rugh et al., 1998b). Grafting experiments with various combinations of wild-type and MerA expressing tobacco shoots and roots suggest plants can be engineered to reoxidize Hg(0) to Hg(II) in leaves and hyperaccumulate mercury above ground. Experiments with MerA expressing rice plants suggest that ionic mercury species can be remediated from aquatic environments to block it conversion to organic forms like methyl mercury.

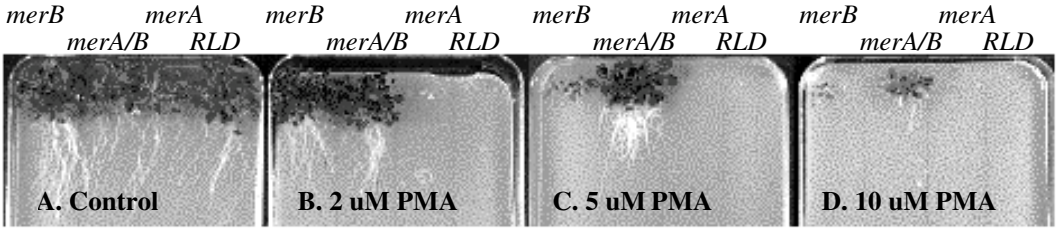
Methyl mercury (MeHg) produced by native bacteria at mercury-contaminated wetland sites is a far more serious problem than Hg(II). MeHg is inherently more toxic than Hg(II), is efficiently biomagnified by several orders of magnitude in the food chain, and poses the most immediate threat to animal populations. MeHg is responsible for the vast majority of cases of mercury poisoning from mercury contaminated fish. In order to eliminate the threat from this toxin in the environment, we have engineered two plant species, *Arabidopsis* and tobacco with a modified bacterial organomercurial lyase gene (*merB*) to degrade methyl mercury and other forms of organic mercury (PMA) to the less toxic Hg(II) (Bizily et al., 1999). Many of the plants examined are highly resistant to levels of MeHg far beyond the levels ever recorded in the environment. Plants expressing both *merA* and *merB* are resistant to even higher levels of MeHg and are capable of efficiently converting MeHg to Hg(0) at levels 1000 time faster than control plants (Bizily et al., 2000) as shown in the figure below. An extensive array of molecular physiology experiments are underway to characterize the expression of *merA* and *merB* in transgenic plants. Our work suggests that native macrophytes (e.g., trees, shrubs, grasses) can be engineered to thrive on and detoxify the most abundant forms of ionic and organic mercury at polluted sites (Rugh et al., 1999; Meagher, 2000).

Our working hypothesis for future research is that transgenic plants expressing the bacterial *merB*

and *merA* genes will a) remove mercury from polluted sites and b) prevent MeHg from entering the food chain. This hypothesis is being tested by focusing our research on three Specific Aims: (1) to test the mechanisms and efficiency of ionic mercury removal from media and soil by transgenic plants expressing various *merA* gene constructs; (2) to test the ability of transgenic plants expressing *merB* and/or *merA* to degrade MeHg and prevent the release of MeHg from mercury-contaminated sediment; and (3) to engineer plants that extract mercury from soil and water and hyperaccumulate mercury and other toxic metals above ground in leaves and stems.

Transgenic *Arabidopsis* seeds and plants expressing *merA* and *merB* together (*merA/B*) are more resistant to organic mercury (PMA) than wild-type plants (*RLD*) or transgenic plants expressing *merA* or *merB* alone. 10 uM = 2 ppm. Figure taken from Bizily et al. (2000).

Publications



Bizily, S., Rugh, C.L., and Meagher, R.B. **(2000). Efficient phytodetoxification of the environmental pollutant methyl mercury by engineered plants. Nature Biotech.** 18**, 213-217.**

Bizily, S., Rugh, C.L., Summers, A.O., and Meagher, R.B. **(1999). Phytoremediation of methyl mercury pollution: *merB* expression in *Arabidopsis thaliana* confers resistance to organomercurials. Proc. Natl. Acad. Sci. USA** 96**, 6808-6813.**

Heaton, A.C.P., Rugh, C.L., Wang, N.-J., and Meagher, R.B. **(1998). Phytoremediation of mercury and methyl mercury polluted soils using genetically engineered plants. J. Soil Contam.** 7**, 497-509.**

Meagher, R.B. **(2000). Phytoremediation of toxic elemental and organic pollutants. Curr. Opin. Plant Biol.** in press.**,**

Meagher, R.B., and Rugh, C.L. **(1996). Phytoremediation of heavy metal pollution: Ionic and methyl mercury. In: OECD Biotechnology for Water Use and Conservation Workshop, eds (Cocoyoc, Mexico: Organization for Economic Co-Operation and Development), 305-321.**

Meagher, R.B., Rugh, C.L., Kandasamy, M.K., Gragson, G., and Wang, N.J. **(2000). Chapter 11. Engineered phytoremediation of mercury pollution in soil and water using bacterial genes. In: Phytoremediation of Contaminated Soil and Water, N. Terry, and G. Banuelos, eds (Boca Raton: Lewis Publishers), pp. 203-221.**

Rugh, C.L., Bizily, S.P., and Meagher, R.B. **(1999). Phytoremediation of environmental mercury pollution. In: Phytoremediation of toxic metals: Using plants to clean-up the environment, B. Ensley, and I. Raskin, eds (New York: Wiley and Sons), pp.**

Rugh, C.L., Gragson, G.M., and Meagher, R.B. **(1998a). Toxic mercury reduction and remediation using transgenic plants with a modified bacterial gene. Hort. Sci.** 33**, 12-15.**

Rugh, C.L., Senecoff, J.F., Meagher, R.B., and Merkle, S.A. **(1998b). Development of transgenic yellow-poplar for mercury phytoremediation. Nature Biotech.** 16**, 925-928.**

Rugh, C.L., Wilde, D., Stack, N.M., Thompson, D.M., Summers, A.O., and Meagher, R.B. **(1996). Mercuric ion reduction and resistance in transgenic *Arabidopsis thaliana* plants expressing a modified bacterial *merA* gene. Proc. Natl. Acad. Sci. USA** 93**, 3182-3187.**

Phytoremediation of Ionic and Methyl Mercury Pollution

Project ID: 54837

Dr. Richard B. Meagher, University of Georgia

Research Objective

Our long-term goal is to enable highly productive plant species to extract, resist, detoxify, and/or sequester toxic heavy metal pollutants as an environmentally friendly alternative to physical remediation methods.

Research Progress and Implications

We have focused this phytoremediation research on soil and water-borne ionic and methylmercury. Mercury pollution is a serious world-wide problem affecting the health of human and wild-life populations. Methyl mercury, produced by native bacteria at mercury-contaminated wetland sites, is a particularly serious problem due to its extreme toxicity and efficient biomagnification in the food chain. We engineered several plant species (e.g., *Arabidopsis,* tobacco, canola, yellow poplar, rice) to express the bacterial genes, *merB* and/or *merA*, under the control of plant regulatory sequences. These transgenic plants acquired remarkable properties for mercury remediation. 1) Transgenic plants expressing *merB* (organomercury lyase) extract methyl mercury from their growth substrate and degrade it to less-toxic ionic mercury. They grow on concentrations of methyl mercury that kill normal plants and accumulate low levels of ionic mercury. 2) Transgenic plants expressing *merA* (mercuric ion reductase) extract and electrochemically reduce toxic, reactive ionic mercury to much less toxic and volatile metallic mercury. This metal transformation is driven by the powerful photosynthetic reducing capacity of higher plants that generates excess NADPH using solar energy. MerA plants grow vigorously on levels of ionic mercury that kill control plants. Plants expressing both *merB* and *merA* degrade high levels of methyl mercury and volatilize metallic mercury. These properties were shown to be genetically stable for several generations in the two plant species examined. Our work demonstrates that native trees, shrubs, and grasses can be engineered to remediate the most abundant toxic mercury pollutants. Building on these data our working hypothesis for the next grant period is that transgenic plants expressing the bacterial *merB* and *merA* genes will (a) remove mercury from polluted soil and water and (b) prevent methyl mercury from entering the food chain. Our specific aims center on understanding the mechanisms by which plants process the various forms of mercury and volatilize or transpire mercury vapor. This information will allow us to improve the design of our current phytoremediation strategies. As an alternative to volatilizing mercury, we are using several new genes to construct plants that will hyperaccumulate mercury in above-ground tissues for later harvest. The Department of Energy's Oak Ridge National Laboratory and Brookhaven National Laboratory have sites with significant levels of mercury contamination that could be cleaned by applying the scientific discoveries and new phytoremediation technologies described in this proposal. The knowledge and expertise gained by engineering plants to hyperaccumulate mercury can be applied to the remediation of other heavy metals pollutants (e.g., arsenic, cesium, cadmium, chromium, lead, strontium, technetium, uranium) found at several DOE facilities.

Characterization of a New Family of Metal Transport Proteins

Project ID: 60271

Mary Lou Guerinot, Dartmouth College

David Eide, University of Missouri at Columbia

Research Objective

Soils at many DOE sites are contaminated with metals and radionuclides. Such soils obviously pose a risk to human and animal health. Unlike organic wastes, which can be metabolized, metals are immutable and cannot be degraded into harmless constituents. Phytoremediation, the use of plants to remove toxic materials from soil and water, may prove to be an environmentally friendly and cost effective solution for cleaning up metal-contaminated sites. The success of phytoremediation will rely on the availability of plants that absorb, translocate, and tolerate the contaminating metals. However, before we can engineer such plants, we need more basic information on how plants acquire metals. An important long term goal of our research program is to understand how metals such as zinc, cadmium and iron are transported across membranes. Our research is focused on a new family of metal transporters, which we have identified through combined studies in the yeast *Saccharomyces cerevisiae* and in the model plant *Arabidopsis thaliana*. We have identified a family of 24 presumptive metal transport genes in a variety of organisms including yeast, trypanosomes, plants, nematodes, and humans. This family, which we have designated the "*ZIP*" genes, provides a rich source of material with which to undertake studies on metal transport in eukaryotes.

Research Progress and Implications

We are currently in year two of a three-year project. IRT1, a member of the ZIP family of transporters, is expressed in the roots of iron-deficient plants and can rescue an iron uptake mutant of yeast. It is not, however, exclusively an iron transporter, as it can also transport zinc, manganese and cadmium when expressed in yeast (Korshunova et al., 1999). In order to determine which residues of IRT1 are involved in substrate recognition and transport, single amino acid changes were introduced into IRT1, replacing various charged residues that were likely to be metal ligands. Two mutations had a significant effect on the functional characteristics of the transporter. One mutant, E103A, transports iron, manganese and cadmium but not zinc and another, D100A, transports zinc and cadmium but no longer transports iron or manganese. Both of these residues, E103 and D100, are predicted to be within an extracellular loop, suggesting that this loop is involved in metal recognition. Such information may allow us to construct transgenic plants in aid of phytoremediation that can specifically accumulate one cation while excluding others.

Transgenic plants expressing IRT1 from the CaMV 35S promoter only accumulate IRT1 protein in the roots of iron-deficient transgenic plants. We believe that IRT1 protein is rapidly turned over unless plants are truly iron-deficient, based on our observations on the behavior of ZRT1 in yeast. ZRT1 is subject to post-transcriptional regulation such that its activity is reduced in the presence of high substrate concentrations. Our recent studies have defined the mechanism of this regulation and demonstrated that down-regulation of the transporters is mediated by zinc-induced endocytosis and vacuolar degradation of the protein (Gitan et al., 1998). We have further characterized the signal transduction pathway that controls ZRT1 endocytosis in response to zinc. Our results establish that ubiquitination is an essential part of the pathway that leads to the endocytosis of ZRT1 in response to zinc. This conclusion is based on the following observations. First, we have established that ZRT1

is mono- and di-ubiquitinated in response to zinc treatment. Moreover, we have shown that this ubiquitination occurs prior to endocytosis; the ubiquitinated protein accumulates in zinc treated mutant cell lines that are blocked for endocytosis. Given that transporter activity does not greatly decrease in these mutants, it appears that ubiquitin addition does not directly interfere with their zinc uptake function. Second mutations that impair components of the ubiquitin conjugation pathway also impair ZRT1 ubiquitination and endocytosis. Specifically, mutations in the functionally overlapping UBC4 and UBC5 E2 ubiquitin conjugating enzymes and the RSP5/NPI1 E3 ubiquitin protein ligase are defective in these processes. These components are known to provide substrate specificity to the ubiquitination process and, consistent with this, other E2 and E3 mutants have no effect on zinc-induced ZRT1 endocytosis. Third, a mutation within ZRT1 that alters a potential ubiquitination site eliminates both ubiquitination and endocytosis. Ubiquitin is conjugated to lysine residues in target proteins and lysine 195 of ZRT1 is the apparent site of ZRT1 modification. These data, combined with the studies of others showing that ubiquitin serves as a tag for endocytosis of other plasma membrane proteins, demonstrate the important role of this modification in signaling endocytosis.

We have also begun studies on the human members of the ZIP family. hZIP2 expression has been observed in uterine epithelial cells (where it is induced by contact inhibition), infant brain, and prostate (based on the EST dbase). hZIP1 appears to be much more widely expressed. hZIP2 is 22% identical and 53% similar to IRT1. We have expressed hZIP2 cells in K562 erythroleukemia cells from the CMV promoter and find that it significantly increases (3-fold) zinc uptake activity. Immunofluorescence experiments using a functional epitope tagged gene demonstrate plasma membrane localization.

Planned Activities

During the next year, we will begin analysis of additional transgenic plant constructs, including *IRT1* plants carrying mutations predicted to eliminate feedback inactivation, and sense and antisense constructs for *ZIP1*, *ZIP2* and *ZIP3*. We will also continue our structure-function studies. In yeast, we will determine if intracellular or extracellular zinc is the signal for endocytosis of ZRT1 and we will identify the region of ZRT1 that serves as the zinc sensor. We will also begin a screen for EMS-generated mutants of the CaMV35S:IRT1 line that have altered sensitivity to cadmium.

Information Access

Eng BH, Guerinot ML, Eide D, Saier MHJ: Sequence analyses and phylogenetic characterization of the ZIP family of metal ion transport proteins. *J. Membr. Biol.* 1998, **166**: 1-7.

Gitan RS, Luo H, Rodgers J, Broderius M, Eide D: Zinc-induced inactivation of the yeast ZRT1 zinc transporter occurs through endocytosis and vacuolar degradation. *J. Biol. Chem.* 1998, **273**: 28617-28624.

Korshunova YO, Eide D, Clark WG, Guerinot ML, Pakrasi HB: The IRT1 protein from *Arabidopsis thaliana* is a metal transporter with broad specificity**.** *Plant Mol. Biol.* 1999, 40: 37-44.

Guerinot ML, Eide D. Zeroing in on zinc uptake in yeast and plants. Curr. Opin. Plant Biol. 1999, **2**: 244-249

Plant Rhizosphere Effects on Metal Mobilization and Transport

Project ID: 55118

Teresa W.-M. Fan, University of California

Richard M. Higashi, University of California
David E. Crowley, University of California

Research Objective

This project addresses phytoremediation of subsurface metal contamination. We are generating fundamental knowledges on how plants mobilize and sequester heavy metals from soils. This information should be applied to facilitating the design of both phytoextraction and stabilization of heavy metals in the subsurface zone.

This project seeks to obtain a mechanistic understanding of mobilization and sequestration of heavy metal ions by plants via root exudation.

Research Progress and Implications

As of Feb, 2000, our work has focused on examining the influence of important rhizosphere factors (i.e. root exudation chemistry and soil organic matter) on metal ion sequestration and plant metabolism in crop plants such as barley, wheat, and rice. In order to understand the chemistry involved in metal ion mobilization by plants, we developed advanced NMR methodology in combination with GC-MS for a comprehensive profiling of root exudates[1], which has been a difficult challenge by conventional approach. Using a similar approach, the intracellular profiles of metal reactive compounds (MRC) in plants are also acquired, which is important to the understanding of how metal ions are sequestered within plants. Moreover, we have completed the development of a convenient gel electrophoretic method for characterizing tissue thiol-rich peptides (important to sequestration of Cd and other pollutant metals). These methodologies have been applied to investigate the relationship between MRC production and metal ion sequestration as a function of plant species, wheat genotypes, transition metal and Cd treatments, as well as soil organic matter (SOM). Experiments had the emphasis on wheat since a full set (7) of Chinese Spring (CS) genotypes (each with one chromosome addition from the salt and Al-tolerant European saltgrass, *Lophopyrum* sp.) are available from Dr. J. Dvorak, UC Davis. Utilizing these and other recombinant wheat genotypes, functional genomic maps are now being generated by Dr. Dvorak as part of an NSF-funded functional genomic center.

The root exudate profiles differed both qualitatively and quantitatively among barley, CS wheat, and rice plants (Figure 1). Under Fe deficiency, the family of mugineic acid (MA) phytosiderophores (PS) were among major components in barley and wheat exudates but was below NMR detection in rice exudate. The barley and wheat exudates were also generally higher in MRC (e.g. amino and organic acids) concentrations. These differences may be related to a better ability of barley and wheat to extract Fe than rice plant.

The increase in exudation of mugineic acids (MAs) under Fe deficiency in barley (3-*epi*-hydroxy-MA, MA, and 2'-DMA) and CS wheat (2'-deoxymugineic acid, 2'-DMA) is consistent with their role in Fe acquisition. The MAs may also be involved in the sequestration of Cu, Zn, and Mn. However, the MAs exudation were not correlated with Cd acquisition by either barley or wheat plants. This is contrary to the general notion that PS may mediate heavy metal uptake by plants. In addition, the Cd treatment caused a large increase in the sequestration of transition metals into wheat, which was not related to root MRC exudation. This Cd effect is not generally known and may be due

to a disrupting effect of Cd on root membrane. It is also possible that some MRC may inhibit rather than enhance metal ion uptake, then the Cd-elicited decrease in exudation may alleviate this inhibition, and results in increased metal sequestration into plant tissues.

In addition to root exudation, the role of SOM (e,g, humics, a prominent class of soil MRC) in metal ion sequestration has been investigated. This information is grossly lacking but necessary for understanding metal ion mobilization and sequestration in the soil environment. The analysis to date indicates that humate plus Cd treatment of CS wheat plants greatly enhanced sequestration of transition metals in roots. This result is contrary to the expected role of humates as a competitive chelator for metals ions. It is likely that soil humates may directly mediate metal ion uptake via their cotransport with metal ions into wheat roots. This is supported by the stimulating effects of humate on MRC metabolism in wheat plants.

We have also begun to characterize the 8 wheat genotypes plus the CS parent for their difference in capacity of metal sequestration and root exudation profile. Analysis to date indicates that the genotypic profile of Cd sequestration differed from those of the transition metals and that the metal sequestration system in wheat may reside on at least two chromosomal loci[2].

The MRC involved in intracellular sequestration of Cd(II) was investigated using the recently developed method that combined fluorescent tagging of thiol-rich peptides by bromobimane with SDS-PAGE. This method allowed a fast and simultaneous assay of both phytochelatins (PC) and metallothionein (MT)-like proteins, as illustrated for wheat, rice, and clam in Figure 2. For both wheat and rice, Cd treatments induced a large accumulation of PC (<3.5 kD SH-rich peptides) but not MT in root and shoot. The PC accumulation was sensitive to Cd sequestration only. These PC appeared to have high affinity for Cd and Pb, as revealed by capillary electrophoresis coupled with ICP-MS. These results suggests PC's role in sequestering heavy metals, particularly in roots where much higher amounts of Cd were sequestered than in shoots.

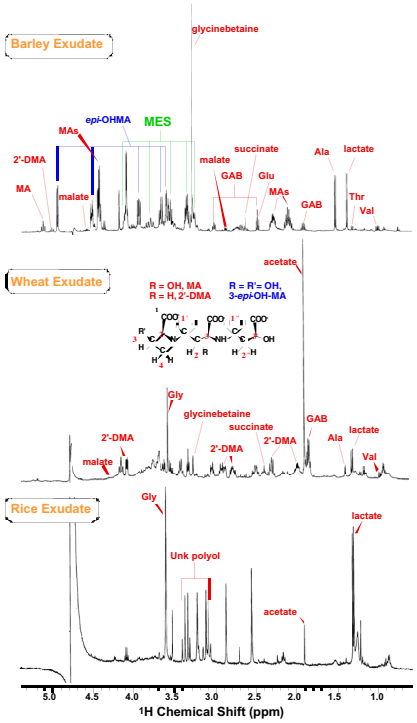


Figure 1. ¹H NMR spectra of whole root exudates from barley, wheat, and rice under a combined Fe deficient and Cd treatment. GAB, γ-amino-butyrate; MES, morpholino-ethanesulfonate; *epi*-OHMA, *epi*-hydroxy mugineic acid; 2'-DMA, 2'-deoxy-mugineic acid; Unk polyol, unknown polyol.

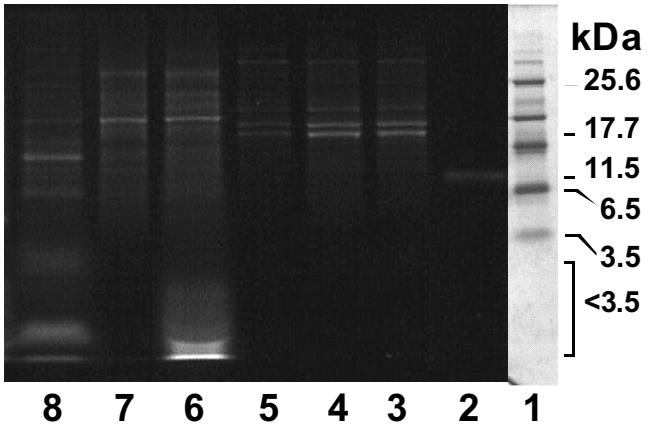


Figure 2. SDS-PAGE of bromobimane-tagged SH-rich peptides and proteins from wheat, rice, and clam tissues. Lanes 1, MW standards; 2, rabbit metallothionein (MT); 3-5, clam MT extracts; 6,7, Cd-treated and control wheat root extracts; 8, Cd-treated rice shoots, respectively.

In conclusion, our results indicate that both non-peptidic MRC and SH-rich peptides may be important to heavy metal sequestration in plant tissues. They may all contribute towards plant's ability to tolerate high levels of metal accumulation and govern subsequent fate of metals in the soil environment. In addition, plant roots sequestered a high amount of metals, which will not be practical to remove from soils by harvest. From the phytoremediation standpoint, the long-term fate of these metals including bioavailability and leachability will need to be addressed. Depending on their speciation and interaction with soil organic matter and minerals, pollutant metals may be "entombed" with aging. Such aging process, if understood, may be enhanced to facilitate subsurface phytoremediation of metal contaminants.

1. Fan, T.W.-M., J. Pedler, A.N. Lane, D. Crowley, and R.M. Higashi, Comprehensive Analysis of Organic Ligands in Whole Root Exudates Using NMR and GC-MS, *Analytical Biochemistry* 251, 57-68 (1997)
2. Fan, T.W.-M., F. Baraud, and R.M. Higashi, Genotypic Influence on Metal Ion Mobilization and Sequestration via Metal Ion Ligand Production by Wheat. To be published in ACS/EMSP Symposium book.

Dynamics of Coupled Microbial and Contaminant Transport

Project ID: 54681

Timothy R. Ginn, University of California

Ellyn M. Murphy, Pacific Northwest National Laboratory
Madilyn M. Fletcher, University of South Carolina
John H. Cushman, Purdue University

Research Objectives

The general problem addressed is the subsurface contamination by chlorinated solvents, and the remediation of chlorinated hydrocarbon contamination by anaerobic consortium involving microbiological agents that undergo transport and growth. This project has potential practical relevance to improved knowledge about how subsurface anaerobes interact dynamically *in situ*, and about how we can control subsurface conditions in order to manipulate the transport properties of microbes, thus allowing controlled mobility to and throughout contaminated regions, and/or controlled immobilization in the preparation of *in situ* biobarriers.

Dynamic microbial attachment/detachment occurs in subsurface systems in response to changing environmental conditions caused by contaminant movement and degradation. This project's objective is to develop the understanding of the environmental conditions and mechanisms by which anaerobic bacteria partition between aqueous and solid phases. In particular this interdisciplinary research project provides fundamental information on the attachment/detachment dynamics of anaerobic bacteria in heterogeneous porous media under growth and growth-limiting conditions. This is a critical requirement for designing and evaluating in situ bioremediation efforts.

Research Progress and Implications

This large-scale multidisciplinary project has made advances in basic and applied sciences on a number of research fronts relevant to the coupled subsurface fate and transport of chlorinated hydrocarbons and the anaerobic microbes involved in their remediation. Progress is reported from the smallest scale upwards, beginning with reaction kinetics modeling for our consortium, and attachment/detachment experiments in parallel, and through our results on reactive transport in natural media, to large scale field remediation results.

The mechanisms controlling degradation by a three-member consortium of anaerobic dechlorinating microorganisms (involving *Desulfomonile tiedjei, Desulfovibrio* (G-11), and *Syntrophobacter wolfei*) were unified and formulated into a mathematical model of the complete reaction system (Chilakapati et al, 1998) and that is fundamentally based on reaction energetics (Brugato, 2000). Explicit accounting of reaction energies allows for consistent treatment of end-product (hydrogen) inhibition of growth and degradation, as well as an accounting of maintenance energy requirements that is crucial for our consortium.

The interaction of microbes in this consortium affects their transport behaviour in ways previously unknown; experiments at the University of S. Carolina utilizing both batch and microflow chamber (http://www.baruch.sc. edu/robb/) conditions have been completed that identify important differences between transport properties of consortium members, as well as significant dependencies of these properties on microbial growth (Van Schie and Fletcher, 1999). Measurements of transport of cells through hydrophobic-interaction and electro-static-interaction columns indicated that all species had negatively charged cell surfaces and that *D. tiedjei* and G-11 possessed some hydrophobic cell surface

properties. Starvation greatly decreases adhesion of *S. wolfei* and *Desulfovibrio* sp. strain G11 but seems to have less of an effect on the adhesion of the other bacteria. The presence of Fe 31 on the substratum significantly increased the adhesion of *S. wolfei*, whereas the presence of silicon hydrophobic groups decreased the numbers of attached cells of all species. Preliminary modeling of these effects is reported in Smits and Cushman (1999a, 1999b).

The interactions of the contaminant with the degrading culture *in situ* depends greatly on the transport processes in the subsurface that control the availability and residence-time of contaminant as substrate for consortium activity and growth (Murphy and Ginn, 2000). These processes include diffusive mass transfer of solute contaminant into low-conductivity regions (Basagaoglu et al., 1999), that commonly defeats remediation strategies that rely on pumping to remove contaminants for biobarrier or *ex situ* remediation. Basagaoglu et al (1999) develop a new simplified modeling approach for keeping track of solute diffusion effects in such media, as it affects the availability of solute hydrocarbon for anaerobic degradation. Field-scale transport in the subsurface involves uncharacterized heterogeneities in physical and chemical properties governing flow and transport (Cushman and Hu, 1997; Ginn, 1998; LaViolette et al., 1999; Cushman and Ginn, 2000), and upscaling the biodegradation processes here requires careful treatment of the dynamic couplings between flow, transport, growth, and bacterial adhesion; a field-scale modeling framework for this is provided through streamtube-ensemble modeling approach (Ginn, 2000) that approximates transport in the field via use of a series of streamtubes. The streamtube approximation allows the reduction in the dimensionality of the problem from three-dimensions to (a series of) one-dimensional effective streamtubes. It also allows the modeling to rely on realistically-available field data such as tracer test results, as opposed to requiring the complete map of the subsurface flow properties (e.g., hydraulic conductivity and porosity) which is never available. Finally, this approach is extended for applicability to our consortium by keeping track of the complete reaction network describing growth, degradation, and bacterial adhesion (Murphy and Ginn, 2000).

A brief summary of implications determined under this research project is as follows: anaerobe transport properties vary in a describable fashion with activity level and degradation; *S. Wolfeii* in particular increases its mobility dramatically under oligotrophic conditions; *D. tiedjeii* generally forms a biofilm under all conditions studied; the presence of *D. tiedjeii* increases the attachment of other consortium members. Anaerobe degradation rates are in fact affected by end-product inhibition and maintenance requirements under commonly encountered subsurface conditions, and a model of these effects is developed. The combined effects of growth-couplings to bacterial transport, and solute substrate fate and transport in natural systems has dramatic implications for bioremediation planning and natural attenuation. In particular, diffusive mass transport into low-conductivity zones limits the availability of solute to *S. Wolfeii* which under starving conditions will decrease its attachment rate and be transported away by convection; amending the groundwater with alternative electron-acceptors and/or with other microbial species can ameliorate this problem. To complement these results, models have been developed for the reaction kinetics, for the development of biofilms and other residence-time effects on bacterial adhesion, for transport in heterogeneous flow fields, and for complete fate (e.g., reaction systems) and transport in the field as arises in *in situ* remediation planning and simulation.

Planned Activities

The project is continuing to the end of the 2000 calendar year via no-cost extensions, and will complete the final experiments allowing exercise and validation of the streamtube-ensemble modeling incorporating both the biodegradation kinetics and the bacterial adhesion interactions identified among members of our consortium. As part of the experimental planning, a large intermediate-scale flow chamber was constructed and is available at PNNL. The intermediate-scale experiments will build on column experiments already conducted by Dr. Murphy at PNNL that show consistent behaviour of the consortium member adhesion dependencies on growth as previously identified in Dr. Fletcher's laboratory -the modeling and manuscript preparation from these column experiments is underway, and the modeling and reporting of the intermediate-scale experiment will conclude project work at the end of the calendar year.

Information Access

Web Pages

http://www.baruch.sc.edu/robb/ details construction of and experiments involving microflow chamber for observing anaerobe adhesion under different growth conditions.

http://www.math.purdue.edu/~jcushman/jcushman.html#dispersion summarizes continuing research on contaminant transport behaviour in natural subsurface environments.

Publications - Papers

Basagaoglu, H., T. R. Ginn, B. J. McCoy, M. A. Marino, A linear driving force approximation to a radial diffusive model, submitted, *Am. Inst. Chem. Eng. J.*, December 1999.

Brugato, C. J., Mathematical Modeling of an Anaerobic Syntrophic Butyrate-Degrading Coculture, Master of Science Thesis, Department of Civil and Environmental Engineering, University of CA, Davis, March, 2000.

Chilakapati, A., T.R. Ginn, and J Szecsody. An analysis of complex reaction networks in groundwater modeling, *Water Resources Research*, 34:1767-1780, 1998.

Cushman, J. H. and T. R. Ginn, The fractional ADE is a classical mass balance with convolution-Fickian flux, submitted, *Water Resources Research*, February 2000.

Cushman, J. H., and B. X. Hu. 1997. Solutions to the stochastic transport problem of $O(\sigma^2_v)$ for conservative solutes. *Stochastic Hydrology and Hydraulics* 11:297-302.

Emerick, R. W., F. J. Loge, T. R. Ginn, and J. L. Darby. Modeling the Inactivation of coliform bacteria associated with particles, submitted, *Water Env. Res*., August 1999.

Ginn, T. R., Streamtube-ensemble techniques for nonlinear multicomponent reactive transport in heterogeneous media, in R. Govindaraju (ed.) Stochastic Methods in Subsurface Contaminant Hydrology, ASCE, in press, 2000.

Ginn, T.R. Comment on "Stochastic analysis of oxygen-limited biodegradation in three dimensionally heterogeneous aquifers," by F. Miralles-Wilhelm, L. W. Gelhar, and V. Kapoor, *Water Resources Research*, 34(9):2423-2426, 1998.

LaViolette, R. A., M. E. Watwood, T. R. Ginn, and D. L. Stoner, Spatial disorder and degradation kinetics in intrinsic biodegradation schemes, *J. Physical Chem A*, 103(23): 4480-4484, 1999.

Moroni, M., and J. C. Cushman, Using Statistical Mechanical Theories in Conjunction with 3D-PTV Experiments to Study Pre-asymptotic Dispersion of a Conservative Tracer in Porous Media, submitted, *Water Resources Research*, September 1999.

Moroni, M., and J. C. Cushman, 3D-PTV Studies of Asymptotic Limits to Classical Stochastic Theories of Porous Media Transport, submitted, *Water Resources Research*, September 1999.

Murphy, E. M. and T. R. Ginn. Modeling microbial processes in porous media, , *Hydrogeology J*., vol. 8 no. 1, pages. 142-158, 2000.

Smits , R.G. and J. H. Cushman, A Random Walk Model for Microbial Dynamics in Porous Media, Part I, submitted July 1999a, *Chem. Eng. Sci.*.

Smits , R.G. and J. H. Cushman, A Random Walk Model for Microbial Dynamics in Porous Media, Part II, submitted July 1999b, *Chem. Eng. Sci.*.

Van Schie, P. M. and M. Fletcher, Adhesion of Biodegradative Anaerobic Bacteria to Solid Surfaces, *Applied and Environmental Microbiology*, Vol. 65, No. 11, p. 5082–5088, Nov. 1999.

Publications - Abstracts/Posters Selection (only a subset shown for space savings)

Murphy, E. M., B. D. Wood, T. R. Ginn, J. H. Cushman, R. Smits, Y. Gorby, M. F. Romine, K. B. Wagnon, 1998. Tracking the Transport of Dissimilatory Iron-Reducing Bacteria in Porous Media by Confocal Microscopy, AGU Fall Meeting, San Francisco, CA, December, 1998, EOS Trans., 79(45):F325.

Ginn, T. R., T. D. Scheibe, E. M. Murphy, M. F. DeFlaun, T. C. Onstott, 1998, Effects of chemical heterogeneity on subsurface fate and transport involving biotic reaction systems: Two Examples. AGU Fall Meeting, San Francisco, CA, December, 1998, EOS Trans., 79(45):F294.

Murphy, E. M., T. R. Ginn, F. J. Brockman, and D. R. Boone, 1997. Growth Effects on the Partitioning and Transport of Bacteria, AGU Fall Meeting, San Francisco, CA, Dec. 1997, EOS Trans., Vol 78 (46), pp F231.

Van Schie, P.M. , M. Fletcher, "Characterization of the adhesive behavior of anaerobic bacteria with bioremediation potential". Poster presented at the American Society for Microbiology Annual Meeting, May 30-June 3, 1999, Chicago, Illinois.

Van Schie, P.M. , D.R. Boone, M. Fletcher, "Adhesion of biodegradative anerobic bacteria to solid surfaces." Poster presented at the American Society for Microbiology Annual Meeting, May 17-21,1998, Atlanta, GA.

Genetic Analysis of Stress Responses in Soil Bacteria for Enhanced Bioremediation of Mixed Contaminants

Project ID: 55031

Kwong-Kwok Wong, Pacific Northwest National Laboratory

Research Objective

The purpose of this project is to provide fundamental knowledge on environment stress response of subsurface bacteria and a radiation-resistant bacterium *(Deinococcus radiodurans)*. This information will be particularly useful in the development of successful bioremediation strategies. These organisms represent two phylogenetically distinct groups of soil bacteria, each of which has specific features of interest for bioremediation. The subsurface bacteria, *Sphingomonas* spp (Savannah River Site), have unique degradative capabilities of organic waste. The study of subsurface bacteria will serve as a model for bioremediation using indigenous bacteria. *D. radiodurans* exhibits high resistance to external stress such as ionizing radiation and organic solvent. The study of *D. radiodurans* will serve as a model for the use of genetically engineered bacteria for bioremediation.

Research Progress and Implications

This report summarizes the work that has been accomplished after the completion of a 3-year project, which started in October 1996. In our past 3-year studies, we have chosen two different bacteria as models for the understanding their genetic responses to starvation and solvent. One of the model organisms, *Deinococcus radiodurans*, is a stress-resistant bacterium. We have identified several genes that respond to organic solvent and starvation, as well as several genes that are required for oxidative or radiation resistance (Markillie et al., 1999). The other model organism is *Sphingomonas aromaticivorans*, which is a subsurface bacterium with a 184 kb catabolic plasmid, and is able to degrade many organopollutants. We have completely sequenced the 184 kb catabolic plasmid (Wong et al., 1996; Romine et al., 1999), and were able to identify many genes involved in the degradation of organopollutants as well as genes related to the conjugative transfer of this plasmid to other bacteria. The solvent inducible genes will be useful for enhancing the solvent resistance of pollutant degrader such as *Sphingomonas aromaticivorans* strains, while the availability of the catabolic plasmid pNL1 will be useful for enhancing the pollutant degradative capabilities of *D. radiodurans*.

To identify solvent-inducible genes, total RNA was extracted from *D. radiodurans* that have been treated with xylene, trichloroethylene, or toluene. An RNA fingerprinting technique was used to identify the RNA transcripts that were induced by solvent. Four putative solvent-inducible genes were identified and were cloned. Two of these genes were found to be the rhamnosyl transferase and methyl transferase by sequencing analysis; the other two genes were unknown. Since the sensitivity of bacteria to solvent is related to their cell surface hydrophobicities, it is possible that these induced genes may be involved in changing the cell surface hydrophobicities. However, further studies are needed to prove that hypothesis. Furthermore, we have also shown that a member associated protein *pspA* is required for solvent resistance.

Using similar strategy, two starvation inducible genes that share sequence homology with *glgX*, glycogen debranching enzyme and *hbd*, 3-hydroxybutyryl coenzyme A dehydrogenase. The enzymes are involved in the utilization of glycogen and fatty acid stored within the cell. The results indicated that *D. radiodurans* might utilize reserved glycogen and fatty acid during starvation condition. This may also explain the difference in fatty acid profile between starved bacteria and normal bacteria.

Enhanced in situ removal of hazardous wastes by stimulating growth of indigenous bacteria with nutrients is a current strategy for enhanced bioremediation. To test the effect of nutrient supply on

subsurface bacteria, four subsurface bacteria, *Terrabacter* sp. B511, *Arthrobacter* sp. B518, *Sphingomonas aromaticivorans* B522, and *Acinetobacter* sp. B525, were chosen for the study. Strain B522 is an organic degrader; the other strains are not. We found that when high level of nutrient is added to starved bacteria, they respond similarly in growth rate. However, when limiting amount of nutrient is added, B518 is stimulated to multiply with the highest growth rate. Our result indicates that the pollutant degrader may be eliminated if low nutrient supply is used repeatedly when there is a fast-growing bacterial strain in the microbial communities, such as the B518 in our case. The result suggests that stimulating indigenous bacteria for enhancing bioremediation may not be effective but harmful to the environment by depicting useful bacteria. However, further in situ experiments are required to support this hypothesis.

Planned Activities

A proposal was submitted for the following planned activities. 1) we propose to use the fundamental knowledge that we have learned to enhance the capabilities of *Deinococcus radiodurans* and *Sphingomonas* strains for bioremediation. 2) With the complete DNA sequences of pNL1 that we have determined, we propose to study the effect of stresses on the genetic transfer of such catabolic plasmid to other bacteria. 3) Finally, we would like to further investigate how nutrient supply will affect the relative growth of starved subsurface organic pollutant degraders in a microbial community.

Publications

Romine, M., L.C. Stillwell, K.K. Wong, S. J. Thurston, E.C. Sisk, J. D. Saffer, and J. K. Fredrickson. 1999. Complete sequence of a 184.5-kb catabolism plasmid from *Sphingomonas aromaticivorans* strain F199. Journal of Bacteriology 181:1585-1602.

Markillie, L.M., S. Varnum , P. Hradecky, and K.K. Wong. 1999. Targeted mutagenesis by duplication insertion in the radioresistant bacterium *Deinococcus radiodurans*: radiation sensitivities of catalase (*katA*) and superoxide dismutase (*sodA*) mutants. Journal of Bacteriology 181:666-669.

Wong, K.K., L. C. Stillwell, C. A. Dockery, and J.D. Saffer. 1996. Use of tagged random hexamer amplification (THRA) to clone and sequence minute quantities of DNA - application to a 180 kb plasmid isolated from *Sphingomonas* F199. Nucleic Acids Res. 24: 3778-3783.

Mechanisms, Chemistry, and Kinetics of Anaerobic Biodegradation of Cis-Dichloroethene and Vinyl Chloride

Project ID: 54666

Dr. Perry L. McCarty, Stanford University

Dr. Alfred M. Spormann, Stanford University

Research Objectives

Biological reductive dehalogenation of the chlorinated ethenes, tetrachloroethene (PCE) and trichloroethene (TCE) to cis-1,2-dichloroethene (cDCE), vinyl chloride (VC) and then ethene is of great interest both for natural attenuation and engineered remediation of these hazardous contaminants in groundwater. This study was directed towards a better understanding of the factors affecting the rate and extent of conversions of cDCE and VC to ethene, which are generally considered the rate limiting steps in the overall process. The objectives of this study are to (1) determine the biochemical pathways for reductive dehalogenation of cDCE and VC, including identification of the enzymes involved, (2) determine the chemical requirements, especially the type and quantity of electron donors needed by the microorganisms for reductive dehalogenation, and (3) evaluate the kinetics of the process with respect to the concentration of both the electron donors and the electron acceptors (cDCE and VC).

Research Progress and Implications

Progress has been made under each of the three primary objectives. One manuscript related to the first objective, two related to the second objective, and one related to the third objective have been published or are in press. An additional manuscript for each of the second and third objectives has been submitted for publication. Pertinent information is provided in the following under "Project Publications." Findings related to the three objectives are summarized below.

Objective One - Biochemical Pathways and Enzymes

We reported a novel cDCE and VC reductive dehalogenase activity in a highly active, mixed culture (Rosner, McCarty & Spormann, 1997). This enzymatic activity appears to be different from previously observed corrinoid-based reductive PCE dehalogenases because 1) the VC dehalogenase activity can not be inhibited with iodopropane, iodoethane, or iodomethane, inhibitors specific for corrinoid-catalyzed reactions, and 2) the higher chlorinated ethene PCE and TCE are reduced by cell-free extracts of this culture only at rates that are orders of magnitude lower than VC dehalogenation (Rosner, McCarty & Spormann, 1997). We are currently purifying the VC dehalogenase. As starting material, we use cells of the mixed culture that reduces VC to ethene (Rosner, McCarty & Spormann, 1997, see above). Cells of this culture are grown in several 15 liter batches of anaerobic medium containing hydrogen, acetate, yeast extract and VC. Cells are harvested under anoxic conditions, broken by passage through a French pressure cell, and unbroken cells are separated from the cell extract by centrifugation. The VC dehalogenating activity is found associated with the membrane fraction of the cell extract and is partially released by treatment with zwitterionic detergents. The first purification step of the VC dehalogenase is anion exchange chromatography. The VC dehalogenating activity elutes as a single fraction which is further purified by hydrophobic interaction chromatography and gel filtration. Analysis of the proteins present in the active fraction of this

purification step reveals at least 3 protein bands as determined by Coomassie-stained SDS-polyacrylamide gels. We expect that only one additional purification step is required to obtain a pure preparation of the VC dehalogenase. Currently, studies to isolate the VC dehalogenating microorganism are under way.

Objective Two - Chemical Requirements

Use of an appropriate hydrogen level is necessary to favor dehalogenation of chlorinated solvents, such as PCE andTCE in substrate competition with other microorganisms. We examined the competition between dehalogenators and other microorganisms occurring in a benzoate-acclimated dehalogenating methanogenic mixed culture (Yang and McCarty, 1998, 1999a). Results show that the dehalogenators competed best against methanogens and homoacetogens when the hydrogen level was maintained between 2 and 11 nM. The 2 nM hydrogen concentration represents the lower threshold value found here for cDCE dehalogenation. The usefulness of this hydrogen range was further confirmed with both batch fed and continuously fed reactors. In batch studies, three times more ethene was produced from dehalogenation of cDCE using propionate than benzoate as electron donor, while benzoate produced three times more methane than propionate. A three times greater hydrogen utilization efficiency for dehalogenation was obtained with a semi-continuous CSTR than with batch reactors when benzoate was used as substrate because a constant hydrogen concentration in the appropriate range could be maintained with the CSTR. These results suggest different approaches that might be used to favor dehalogenators in competition with other microorganisms.

We also conducted comparative studies with benzoate, propionate, oleate, tetrabutyl orthosilicate (TBOS) and biomass as substrates for dehalogenation of cDCE (Yang and McCarty, 1999b). All five substrates supported dehalogenation. Sufficient calcium was required to precipitate oleate and thus reduce its toxicity to the dehalogenating microorganisms. More cDCE was dehalogenated with TBOS than with benzoate, although TBOS initially had an inhibitory effect. The most efficient dehalogenation was associated with biomass, 20% of which was used for dehalogenation, even higher than the 17% obtained with propionate. Use of biomass as a reaction medium in a permeable reaction barrier system is suggested.

Objective Three - Process Kinetics

Biological reduction of the chlorinated solvents tetrachloroethene (PCE) and trichloroethene (TCE) completely to ethene is of interest for engineered or intrinsic destruction of these prevalent groundwater contaminants. However, the transformations are frequently not complete, leading to the production of vinyl chloride (VC), a more hazardous compound. Factors affecting the relative rates of destruction of the solvents and their intermediate products are thus of interest. We examined the maximum degradation rates (kX) and half-velocity coefficients (K_S) for these chlorinated ethenes used as electron acceptors in reductive dehalogenation with hydrogen in excess using an enrichment culture grown on benzoate, hydrogen, and PCE (Haston and McCarty, 1999). Initial dehalogenation rates were measured at various chlorinated ethene concentrations in batch studies. With 38 mg/L volatile suspended solids of this culture, the kX and 95% confidence intervals for PCE, TCE, cDCE, and VC at 25ºC were found to be 77 ± 5, 59 ± 11, 14 ± 3, and 13 ± 3 µM/day with K_S values of 0.11 ± 0.04, 1.4 ± 0.9, 3.3 ± 2.2, and 2.6 ± 1.9 µM, respectively. The lower maximum transformation rates and higher K_S values for cDCE and VC partly explain why incomplete transformation of PCE and TCE often occurs in the field.

In order to predict the time required for onset of dechlorination following bioaugmentation of a field site, information is needed about the growth rates for the microorganisms involved and the factors affecting dechlorination rates. Studies we recently completed using a mixed PCE-dehalogenating culture indicated that the same species was involved in both cDCE and VC dechlorination, and that cDCE and VC competitively inhibited each other's dechlorethylene rate (Haston, Yang, and McCarty, 1999). The inhibition coefficients for each were similar to their cDCE and VC half-velocity coefficients of 3.3 and 2.6 µM, respectively. Using a Monod-type growth model, the maximum specific growth rate on VC was determined to be 0.21 ± 0.02 /day. Commercial

cDCE was found to inhibit growth of the culture in proportion to the amount added. Biologically generated cDCE, however, exhibited no such adverse affect. Correcting for this inhibition, the maximum specific growth rate for cDCE dechlorination was 0.30 ± 0.06 /day.

Planned Activities

A request for a one-year extension of this grant without additional funds was approved internally by Stanford University. The completion date will now be September 14, 2000. Research under all three objectives is continuing. Under objective one, efforts are being made to purify the dehalogenating enzymes. Under objective two, studies are being conducted to find ways to increase the efficiency of electron donor utilization for dehalogenation. Under phase three, further efforts are being made to quantify the kinetics of dehalogenation, especially for high concentrations of chlorinated solvents where potential toxicity is of great importance.

Project Publications

Haston, Z. C. and McCarty, P. L. 1999. Chlorinated Ethene Half-Velocity Coefficients (K_S) for Reductive Dehalogenation, *Environmental Science and Technology,* **33**(2), 223-226.

Haston, Z. C., Yang, Y., and McCarty, P. L. 1999. Organism Growth and Substrate Utilization Kinetics for the Anaerobic Dehalogenation of cis-Dichloroethene and Vinyl Chloride, submitted for publication .

Rosner B, McCarty PL, Spormann AM 1997: In vitro studies on reductive vinyl chloride dehalogenation by an anaerobic mixed culture. *Appl. Environ. Microbiol.*, **63** (11):4139-4144.

Yang, Y. and McCarty, P. L 1998. Competition for Hydrogen within a Chlorinated Solvent Dehalogenating Mixed Culture, *Environmental Science and Technology* , **32**(22), 3591-3597.

Yang, Y. and McCarty, P. L., 1999a. Response to "Comment on Competition for Hydrogen within a Chlorinated Solvent Dehalogenating Anaerobic Mixed Culture," *Environmental Science & Technology*, In Press.

Yang, Y. and McCarty, P. L. 1999b. Biomass, Oleate, and Other Possible Substrates for Chloroethene Reductive Dehalogenation, submitted for publication.

Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media

Project ID: 55416

Dr. Frederick S. Colwell, Idaho National Engineering and Environmental Laboratory

Research Objectives

The U.S. Department of Energy (DOE) is faced with cleaning up wastes from reactor and weapons production activities during the latter half of this century. Many DOE sites have contaminants that are difficult to access due to depth and complex geology and are challenging to degrade using conventional methods. Fundamental, field-based research is required to understand what is needed to address complex cleanup issues such as those that exist in fracture flow environments. The key objective of this research is to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium with respect to vertical heterogeneities. The research will be performed on samples collected from the Test Area North (TAN) site at the Idaho National Engineering Laboratory (INEL) where a dissolved trichloroethene (TCE) plume is migrating in the Snake River Plain aquifer. To determine whether microbial degradation is spatially correlated to preferred flow paths for the contaminant and required electron donors and acceptors we will characterize the biological and abiological properties of cores and samples from multi-level samplers placed in the same borehole. We will use a combination of traditional microbiological methods (e.g., enrichments) and molecular tools to characterize the indigenous microbial communities. Collaboration with other EMSP investigators studying this site and the DOE Office of Environmental Management (EM40) which is implementing remediation will lead to more complete understanding of the biotic and abiotic processes in the subsurface at TAN. We believe that the fundamental research proposed will explain the distribution of microorganisms that can degrade TCE in the context of the geochemical and physical constraints under which these organisms function. This in turn will allow better decisions to be made with regards to the use of remedial technologies such as natural attenuation and in situ bioremediation at this geologically complex site.

Complete Detoxification of Short Chain Chlorinated Aliphatic Compounds: Isolation of Halorespiring Organisms and Biochemical Studies of the Dehalogenating Enzyme Systems

Project ID: 55105

James M. Tiedje, Michigan State University

Frank E. Löffler, Michigan State University

Executive Summary

The stimulation of halorespiring microorganisms is potentially the most promising and cost-effective technology for remediating sites contaminated with chlorinated solvents. Central to the successful implementation of such a bioremediation technology is the determination of the presence of halorespiring organisms and information on their physiology. Unfortunately, our knowledge of halorespiring microbes that detoxify chlorinated solvents is limited. Hence, our work focused on the isolation and characterization of halorespiring populations, and the initial investigation of the dechlorinating enzyme systems. In addition, tools to evaluate the presence/activity of halorespiring populations in the environment were developed.

Halorespiring enrichment cultures were obtained from a variety of contaminated and non-contaminated sites. Five enrichments completely dechlorinated tetrachloroethene (PCE) to ethene, and four different cultures dechlorinated 1,2-dichloropropane to propene. Hydrogen consumption threshold measurements and the determination of the fraction of electrons going towards reductive dechlorination confirmed the presence of halorespirers. Two halorespiring isolates were obtained: *Desulfuromonas ottawaensis* strain BB1, which dechlorinates PCE to *cis*-1,2-dichloroethene, and *Desulfitobacterium* sp. strain Viet1, which dechlorinates PCE to trichloroethene. *Desulfuromonas ottawaensis* strain BB1 dechlorinated PCE at rates of 150 nmol min^{-1} mg of $protein^{-1}$ with acetate as the electron donor. In cell-free systems PCE was dechlorinated at rates of at least 300 nmol min^{-1} mg of $protein^{-1}$ with methyl viologen as the electron donor. In addition, a defined mixed culture consisting of three populations including a *Dehalococcoides* species was obtained. This mixed culture completely dechlorinated PCE to the environmentally benign product ethene.

Specific primers based on 16S rDNA sequences of *Desulfuromonas ottawaensis* strain BB1 and the *Dehalococcoides* species were designed, and used in a nested PCR approach for the sensitive and specific detection of these organisms in environmental samples. Both dechlorinators were detected in three out of three river sediment samples tested, and two different contaminated aquifers tested positive with the *Desulfuromonas ottawaensis*- and *Dehaloccocoides*-targeted primers, respectively.

Natural attenuation and engineered bioremediation are often the most cost-effective corrective actions for addressing groundwater contaminated with chlorinated solvents. To decide on the most cost-effective and successful bioremediation strategy the presence or absence of halorespiring organisms must be confirmed. The tools developed in this work (measurements of hydrogen consumption thresholds, molecular probes) are relevant for regulatory agencies in order to facilitate decisions on which bioremediation technology (biostimulation or bioaugmentation) is most promising at a particular site. In addition, a better understanding of the physiology of the halorespiring organisms as well as the biochemistry of the dehalogenating enzyme systems enhances our knowledge of how these organisms can successfully be employed in the bioremediation of contaminated sites.

Relevance, Impact and Technology Transfer

Natural attenuation and engineered bioremediation are often the most cost-effective corrective actions for addressing groundwater contaminated with chlorinated solvents. To decide on the most cost-effective and successful bioremediation strategy the presence or absence of halorespiring organisms must be confirmed. The tools developed in this work (measurements of H_2 consumption thresholds, molecular probes) are relevant for site owners and regulatory agencies in order to facilitate decisions on which bioremediation technology (biostimulation or bioaugmentation) is most promising at a particular site. We are currently testing these methods at several state and DoD sites. In addition, a better understanding of the physiology of the halorespiring organisms as well as the biochemistry of the dehalogenating enzyme systems enhances our knowledge of how these organisms can be most successfully employed in the bioremediation of contaminated sites.

High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions

Project ID: 55264

Dr. Ernest L. Majer, Lawrence Berkeley National Laboratory

Dr. Fred J. Brockman, Pacific Northwest National Laboratory

Research Objective

This research is an integrated physical (geophysical and hydrologic) and microbial study using innovative geophysical imaging and microbial characterization methods to identify key scales of physical heterogeneities that affect the biodynamics of natural subsurface environments. Data from controlled laboratory and in situ experiments at the INEL TAN site will be used to determine the dominant physical characteristics (lithologic, structural, and hydrologic) that can be imaged in situ and correlated with the microbial properties. Emphasis will be placed on identifying fundamental scales of variation of physical parameters that control transport behavior relative to predicting subsurface microbial dynamics. A key hypothesis addressed is that nutrient flux and transport properties are key factors in controlling microbial dynamics. The outcome will be an improved understanding of the relationship between physical and microbial heterogeneity, thus facilitating the design of bioremediation strategies in similar environments. The work described here is an extension of current basic research on natural heterogeneity within the DOE/OHER Subsurface Science Program (SSP) and is intended to be one of the building blocks of an integrated and collaborative approach with an INEL/PNL effort aimed at understanding the effect of physical heterogeneity on transport properties and biodynamics in natural systems.

Design and Construction of *Deinococcus radiodurans* for Biodegradation of Organic Toxins at Radioactive DOE Waste Sites

Project ID: 59786

Michael J. Daly, Uniformed Services University of the Health Sciences

James K. Fredrickson, Pacific Northwest National Laboratory
Lawrence P. Wackett, University of Minnesota

Research Objective

Seventy million cubic meters of ground and three trillion liters of groundwater have been contaminated by leaking radioactive waste generated in the United States during the Cold War. A cleanup technology is being developed based on the extremely radiation resistant bacterium *Deinococcus radiodurans* that is being engineered to express bioremediating functions. Research aimed at developing *D. radiodurans* for organic toxin degradation in highly radioactive waste sites containing radionuclides and heavy metals was started by this group in September 1997 with support from DOE EMSP grant DE-FG07-97ER20293.

Research Progress and Implications

This report summarizes work after 2.5 years of a 3-year project dedicated to engineering the radiation resistant bacterium *Deinococcus radiodurans* for biodegradation of organic toxins at radioactive DOE waste sites. Our progress closely matches the Aims proposed in our 1997 EMSP application and is summarized as follows. We have demonstrated that *D. radiodurans* can be genetically engineered for degradation of toxic organic compounds using expression systems that were tested during growth of engineered *D. radiodurans* at 6,000 rad/hour. While *D. radiodurans* is naturally tolerant to the concentrations of uranium and plutonium at most radioactive DOE waste sites, its growth will likely be inhibited by the concentrations of heavy metals at those sites. Therefore, we are cloning metal resistance functions into toxin-degrading *D. radiodurans*. For example, we have cloned the *Escherichia coli merA* locus into engineered *D. radiodurans* strains capable of degrading chlorobenzene, 3,4-dichloro-1-butene, and toluene. These *merA*-containing strains were resistant to highly toxic Hg(II), and could reduce Hg(II) to much less toxic and volatile Hg(0). An assortment of organic toxin-degrading genes is now being tested in *D. radiodurans* in combination with genes encoding resistance to Hg(II), Pb(II), and Cr(VI). Characterization of bioremediating strains was aided by our development of a synthetic minimal medium for *D. radiodurans.* In combination with our genomic informatic analyses, this medium has enabled us to identify the minimum nutrient requirements necessary to support growth in nutrient poor radioactive environments, and to explain how radiation resistance relates to this organism's metabolic repertoire. Together, these studies have facilitated our ongoing experimental efforts to engineer *D. radiodurans* for growth on toxic organic compounds in radioactive environments. It now appears likely that we will be able to engineer *D. radiodurans* to use chlorinated hydrocarbons as carbon/energy sources that could provide electron donors for growth of toxin-degrading *Deinococcus* and, possibly, metal reduction; we have shown that anaerobic cultures of wildtype *D. radiodurans* can reduce U(VI), Tc(VII), and Cr(VI).

Work funded by the existing grant has already contributed to eleven papers on the fundamental biology of *D. radiodurans* and its design for bioremediation of highly radioactive waste environments.

Planned Activities

1) Continue to develop radiation resistant bacteria for toxic organic compound degradation, with primary emphasis on *D. radiodurans*, but also on *Deinococcus geothermalis* that may yield strains more suitable for bioremediation in nutritionally restricted radioactive environments. As an extension of this research we will continue to introduce and evaluate metal resistance genes in organic toxin degrading *Deinococcus* strains.
2) Develop *D. radiodurans* strains capable of utilizing chlorinated hydrocarbons and related compounds as carbon and energy sources for growth and, possibly, metal reduction. Metabolic engineering of *D. radiodurans* will be guided using a combination of genomic informatics and a novel system to evaluate gene expression patterns developed specifically for *D. radiodurans*.
3) Exploiting *D. radiodurans*' prolific genetic recombination capabilities for *in vivo* gene shuffling to generate novel catabolic genes and pathways. *D. radiodurans* containing different, but related, catabolic genes will be irradiated to extremely high levels and allowed to recover. Recombinants will be selected and studied for novel catabolic functions.
4) Evaluate engineered *D. radiodurans* strains for effectiveness at degrading chlorinated hydrocarbons in natural subsurface materials from DOE sites containing organic contaminants and toxic metals.

Information Access

1 C. Lange, L. P. Wackett, K. W. Minton and **MICHAEL J. DALY** (1998) Engineering a recombinant *Deinococcus radiodurans* for organopollutant degradation in radioactive mixed waste environments. *Nature Biotechnology*, **16**, 929-933.

2 H. Brim, S. McFarlan, L. Wackett, K. W. Minton, M. Zhai, J. Fredrickson, and **MICHAEL J. DALY** (2000) Engineering *Deinococcus radiodurans* for metal remediation in radioactive mixed waste environments. *Nature Biotechnology*, **18**, 85-90.

3 **MICHAEL J. DALY** (2000) Engineering radiation-resistant bacteria for environmental biotechnology. *Current Opinion in Biotechnology* **11**, Issue 3, In Press.

4 A. Venkateswaran, S. C. McFarlan, D. Ghosal, K. W. Minton, A. Vasilenko, K. Makarova, L. P. Wackett, and **MICHAEL J. DALY** (2000) Physiologic determinants of radiation resistance in *Deinococcus radiodurans*. *Appl. Environ. Microbiol*. Vol. **60**, In Press.

5 J. K. Fredrickson, H. M. Kostandarithes, A. W. Li, A. E. Pyle, and **MICHAEL J. DALY** (2000) Reduction of Fe(III), Cr(VI), U(VI), and Tc(VIII) by *Deinococcus radiodurans*. *Appl. Environ. Microbiol.* Vol. **60**, In Press.

6 K. S. Makarova, Y. I Wolf, K. W. Minton, O. White, and **MICHAEL J. DALY** (1999) Short repeats and insertional elements in *Deinococcus radiodurans* and comparison to other bacterial species. *Res. Microbiol*., **150**, 711-724.

7 K. S. Makarova, L. Aravind, **MICHAEL J. DALY**, and E. Koonin (2000) Specific expansion of protein families in the radioresistant bacterium *Deinococcus radiodurans*. Submitted to *Genetica*.

8 A. K. Sharma, A. Jambura, M. M. Cox, R. B. Inman, K. W. Minton, and **MICHAEL J. DALY** (2000) Expression and characterization of the RecA protein from the extremely radioresistant bacterium *Deinococcus radiodurans*. Submitted to *J. Biol. Chem*.

9 K. S. Makarova, E. V. Koonin, L. Aravind, L. Tatusov, Y. I. Wolf , O. White, J. R. Battista, and **MICHAEL J. DALY** (2000) The genome of the extremely radioresistant bacterium *Deinococcus radiodurans*: Comparative genomics and applications. *Microbiology and Molecular Biology Reviews*. Invited Review.

10 J. Lin, R. Qi, C. Aston, J. Jing, T. S. Anantharaman, B. Mishra, O. White, K. W. Minton, **MICHAEL J. DALY**, J. C. Venter, and D. C. Schwarzt (1999) Whole genome shotgun optical mapping of *Deinococcus radiodurans* using genomic DNA molecules. *Science*, **284**, 1558-1561.

11 O. White, J. A. Eisen, J. F. Heidelberg, E. K. Hickey, J.D. Peterson, R. J. Dodson, D. H. Haft, M. L. Gwinn, W. C. Nelson, D. L. Richardson, K. S. Moffat, H. Qin, L. Jiang, W. Pamphile, M. Crosby, M. Shen, J. J. Vamathevan, P. Lam, L. McDonald, T. Utterback, C. Zalewski, K. S. Makarova, L. Aravind, **MICHAEL J. DALY**, K. W. Minton, R. D. Fleischmann, K. A. Ketchum, K. E. Nelson, S. Salzberg, H. O. Smith, J. C. Venter, C. M. Fraser (1999) Sequencing and functional analysis of the *Deinococcus radiodurans* genome. *Science*, **286**, 1571-1577.

Molecular Profiling of Microbial Communities from Contaminated Sources: Use of Subtractive Cloning Methods and rDNA Spacer Sequences

Project ID: 55152

Dr. Frank T. Robb, University of Maryland at Baltimore

Research Objective

The major objective of the research is to provide appropriate sequences and to assemble a high-density DNA array of oligonucleotides that can be used for rapid profiling of microbial populations, from polluted areas and from areas of other interest. The sequences to be assigned to the DNA array are chosen from cloned genomic DNA from groundwater at DOE sites containing organic solvents. The sites, Hanford Nuclear Plant and Lawrence Livermore Site 300 (LLNL), have well characterized pollutant histories, which have been provided by our collaborators.

Research Progress and Implications

We are developing microarrays using the 16s ribosomal DNA intergenic spacer regions (ISRs) to profile community composition, for rapid characterization of microbial communities in contaminated ecosystems, and for detection of bacteria carrying pollutant-metabolizing genes. This DNA sequence and our routine methods have been described in our previous reports. Glass slide arrays were made and tested as follows. Hypervariable stretches of the ISRs, in the 16s-to-tRNA-ILE, inter-tRNA (itRNA), and tRNA-ALA- to-23s regions, were synthesized and hybridized against synthetic templates and PCR products corresponding to the opposite strand in collaboration with Orchid (nee Molecular Tool, Inc). Capture probes for silanized glass slide hybridization experiments were modified with a 5' sulfhydryl group for attachment to the slides. Detection probes were modified with 3' fluorescein tags; synthetic templates were unmodified. PCR products were produced using one primer with a 5' fluorescein and four 5' phosphorothioate bonds, followed by 0.5-1 hour at 37˚C in the presence of 1 unit/µL T7 gene 6 exonuclease to make them single stranded. This exonuclease digests double stranded DNA, working from the 5' end of each strand; the strands with the phosphorothioate linkage were therefore resistant to this enzyme.

Arrays on glass slides were made by spotting capture probes and fluorescent marker in 500 mM pH 9 bicarbonate buffer (either 0.1 µL by hand or 30 nL by Hamilton 220 automated pipetting robot), allowing attachment overnight, washing 3 times in TNTw, overlaying with 1 pmol synthetic template or 0-5 pmol PCR product that had been heated in the presence of detection probe 10 minutes at 95˚C and then cooled to 37˚C. Following a 0.5-3 hour hybridization, the slides are washed 3 times in TNTw and scanned on a Molecular Dynamics Fluorimager using a 530 nm filter.

In order to distinguish progress of acetate and nitrate bioremediation in the Hanford area, it appears that 4 sequences (replicated) are all that are required. The data reveal considerable strain variation between sample sites. The distribution of sequences found is striking: From 38 to 45% of the unique sequences are found only once in each level. The presence of three of the common clones, 1.02, 2.04, and 4.01, is correlated with the process of remediation: 1.02 appears at the end, 2.04 early (predominantly), and 4.01 early or in the middle of remediation. These three clones are from pseudomonads, as are 20 of all the bins (according to blastn). Other bins blast best against *Thiobacillus*, *Agrobacterium*, *Bartonella*, *Xanthomonas*, and *Xylophilus*. We assume little PCR bias based on the generality of the primers used and on the use of at least three pairs of primers per sampling site. We are synthesizing diagnostic oligos for as many of the Hanford bins as possible in order to compare

the ISRs found in the LLNL sites, and to establish the microarray method. The optimal time (3 hours) of hybridization and the detection limit (10 fmol) using PCR products of plasmid DNA .

Monitor wells within the LLNL Building 834 Area having varying amounts of VOC contamination are being sampled for groundwater microbiological assessment. Five monitor wells have been selected for this study based on their VOC concentrations. Two of the wells selected (W-834-D3, and W-834-D14) have high VOC concentrations, predominantly TCE, in excess of 100,000 µg/L. A third well (W-834-B3) has lower levels of VOCs, around 10,000 µg/L, which is almost entirely composed of 1,2-DCE. The two remaining wells selected (W-834-S6, and W-834-T5) have not historically contained any VOC compounds (clean wells, control populations). All five wells selected are installed within the same hydrologic unit.

ISRs from 2 LLNL wells have been sequenced, again revealing a striking difference in the bacterial flora between moderate and high VOC levels, as shown in Fig. 1. The more contaminated groundwater appears more diverse at this stage of sequencing. There appear to be several identical signature ISRs at both the Hanford and LLNL sites.

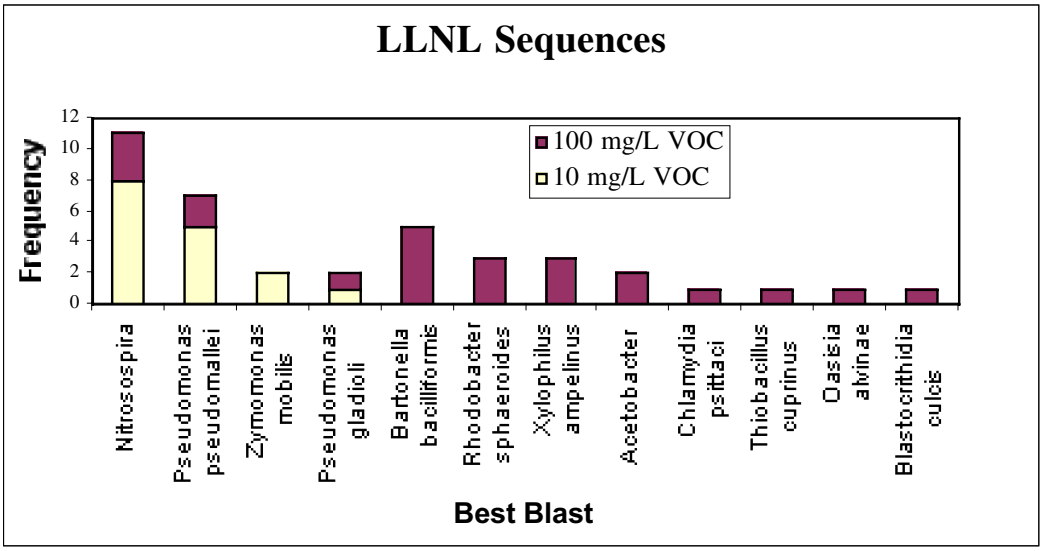


Figure 1. Distribution of ISR sequences in LLNL samples representing high and moderate VOC levels.

Student Training

For the past year Karen Schindler, an undergraduate student from Loyola College working with our collaborator Dr. Mary Lowe, has been sequencing the LLNL samples, both as work-study in the summers and as a research project during the academic year.

Planned Activities

Our data so far from Hanford suggests that diversity does vary greatly with bioremediation and that there are many bacterial ISR sequences that can indicate the effects of bioremediation. We will shortly test the environmental DNA from LLNL (as a PCR amplified sample) in an inter-site hybridization experiment against the sequences from the Hanford sites to determine overlap in microbial community composition between the sites. We will also hybridize against sequences described in the NCBI and Deep Subsurface databases, to probe for sequences without the intermediate cloning step. We have recently made arrangements to acquire more samples from the Hanford site (Evan Dressel, pers. comm.). The samples are from the same geologic strata and include clean well samples. We will test PCR products against the arrays to find which bacterial strains are common to both Hanford areas, and, after subtractive hybridization, concentrate on novel ISRs.

We are also preparing to test the extent of PCR bias by using TaqMan quantitative PCR on the LLNL samples. We have chosen the 3' end of the 16S for one (universal) primer and the probe; the

other (diagnostic) primer will come from the ISR within 150 bases from the first primer. By assembling a distribution of strains from LLNL as from Hanford and running TaqMan experiments on the same samples, we can determine the confidence intervals for ISR copy numbers. Because bacterial communities in groundwater have been a closed book until the advent of molecular techniques, we do not know how diverse these environments can be, and how well molecular techniques describe them.

Acknowledgments and Contact Information

This project is supported by a DOE Environmental Management grant .

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Web Site: http://comb5-156.umbi.umd.edu/bags.html (local ISR database)

An Investigation of Homogeneous and Heterogeneous Sonochemistry for Destruction of Hazardous Waste

Project ID: 54834

Dr. Inez Hua, Purdue University

Research Objective

The primary objective of this research project is to acquire a deeper fundamental knowledge of acoustic cavitation and cavitation chemistry, and in doing so, to ascertain how ultrasonic irradiation can be more effectively applied to environmental problems. The primary objective will be accomplished by examining numerous aspects of sonochemical systems and acoustic cavitation. During the course of the project, the research group will investigate sonochemical kinetics and reactive intermediates, the behavior of heterogeneous (solid/liquid) systems, and the significance of physical variables during sonolysis. An additional component of the project includes utilizing various techniques to image cavitation bubble cloud development.

Research Progress and Implications

This report summarizes results after **3** years of investigation. On-going projects will be summarized in this annual report. Detailed information and results from year 1 and year 2 of this investigation can be found in the publications listed at the end of this report, under the heading "Publications Resulting from This Work".

a. Spectroscopic Stuides of Organic Free-Radicals Resulting from Sonication of Polychlorinated Biphenyls

Cavitation chemistry encompasses complex pathways involving numerous reactive intermediates, and identification of these intermediates is crucial for elucidating the mechanism of sonochemistry. Free - radicals play an important role in the vapor phase chemistry of the bubble, and also in aqueous reactions. For example, it has been reported that $\bullet CH_3$, $\bullet CH_2CH_2OH$, and $\bullet CH_2$-phenyl were produced during sonication of aqueous methanol, ethanol, and sonication of pure toluene.

In order to identify organic free - radicals present at quantifiable concentrations during the sonication of PCBs, we employed Electron Spin Resonance (ESR) with a spin trap, N-*t*-butyl-α-phenyl-nitrone (PBN). PBN reacts with the reactive free - radicals to form more stable spin-adducts, which are then detected by ESR. The ESR spectrum of a PBN spin adduct exhibits hyperfine coupling of the unpaired election with the ^{14}N and the β-H nuclei which leads to a triplet of doublets. The combination of the spin-adduct peak position and peak interval uniquely identifies the structure of a free-radical.

The first-derivative ESR spectra of 2-PCB and 4-PCB yielded interpretable signals, but no significant peaks were found when analyzing sonicated solutions of 2,4,5-PCB. The formation of organic radicals at a detectable level may have been hindered by the low aqueous solubility of 2,4,5-PCB.

Figure 1 is an ESR spectrum acquired after 10 minutes of sonicating an Ar - saturated solution of 2-PCB and PBN at 20 kHz. Samples that were irradiated at different power intensities for the same time period (10 minutes) are compared. Peaks consist of a triplet of doublets with the parameters of $\alpha_H = 4.2$, $\alpha_N = 16.0$, which are characteristic α values for phenyl radical trapped by PBN. These peaks appeared in all ESR spectra obtained from sonicated solutions of 2-PCB (n = 20) and 4-PCB (n = 19) with irradiation times longer than 10 minutes (n = number of experiments).

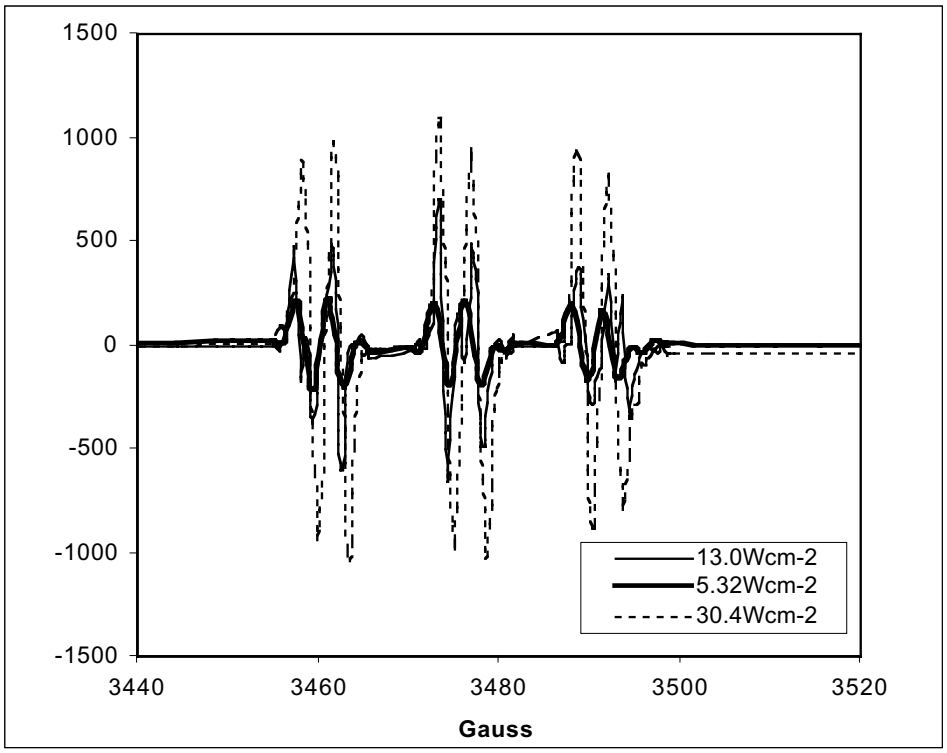

Fig. 1: First - derivative ESR spectrum indicating the accumulation of PBN-phenyl after 10 minutes of sonicating an Ar-saturated solution of 2-PCB (4.6 mM) at 20 kHz and varying sound intensities.

Note that the integrated peak area (intensity) of the signal correlates with the spin adduct concentration, and is therefore proportional to the initial concentration of free radical in solution. At the highest power intensity (30.4 Wcm^{-2}), the peak intensity is highest. This indicates that the rate of formation of phenyl radical, and therefore, thermolytic cleavage of the biphenyl moiety, is accelerated at higher sound intensities. The enhancement can be understood by considering bubble implosion and the resulting conditions within the bubble. Acoustic intensity is directly related to acoustic pressure as described in Equation 1, which in turn determines the final temperatures and pressures within the bubble (Equations 2, 3).

$$I = \frac{P^2}{2\rho C} \tag{1}$$

$$T_{max} = T_o \frac{P_m (k-1)}{P_o} \tag{2}$$

$$P_{max} = P_o \left(\frac{P_m (k-1)}{P_o} \right)^{\left(\frac{k}{k-1}\right)} \tag{3}$$

where I = sound intensity, P = acoustic pressure, r = density of water, C = speed of sound in water. T_{max}, P_{max} = maximum temperature and pressure at implosion, T_0 = ambient temperature of water (22° C in our experiments), P_0 = pressure in bubble at its maximum size (assumed to be the vapor pressure

of water), P_m = peak pressure of the bubble, which is the sum of the hydrostatic and acoustic pressure (P, from Eqn. 1), and k = polytropic index of saturating gas.

Thus, as the sound intensity increases, higher temperatures and pressures exist within the bubble interior, which then enhance the overall decomposition rate of the PCBs. In addition, the formation of organic free - radicals is also enhanced at higher sound intensities. These observations are consistent with previous reports of enhanced decomposition kinetics at higher acoustic intensities.

A second set of ESR experiments highlights the correlation between physico-chemical properties and sonolytic decomposition kinetics. Fig. 2 is a comparison of the first derivative spectra for separate, sonicated solutions of 2-PCB (4.6 mM) and 4-PCB (5.4 mM). Both congeners yield phenyl radical. Note that after 10 minutes of sonication at 30.4 W cm^{-2}, the signal intensity was higher for 2-PCB than for 4-PCB despite the lower initial concentration of 2-PCB. Because the mole ratio of spin-trap (20 mM) was in such large excess compared to either congener, the trapping efficiency was most likely the same for each congener. Also, formation of the phenyl radical involves thermolysis of C-C bond, which can only occur within high temperature regions of the cavitation bubble (the bubble interior, or at the gas-liquid interface), and not within the bulk solution at ambient temperature. Therefore, a faster accumulation of phenyl radical is consistent with the hypothesis that a relatively greater number of 2-PCB (log H = -0.09) molecules partition into the bubble interior compared to 4-PCB (log H = -0.63).

Fig. 3 demonstrates the time variation of the PBN-phenyl spin-adduct accumulation during sonication of 2-PCB. The spin-adduct initially accumulates, corresponding to formation of phenyl radical from the destruction of 2-PCB. Eventually, the intensity of the peak decreases because the

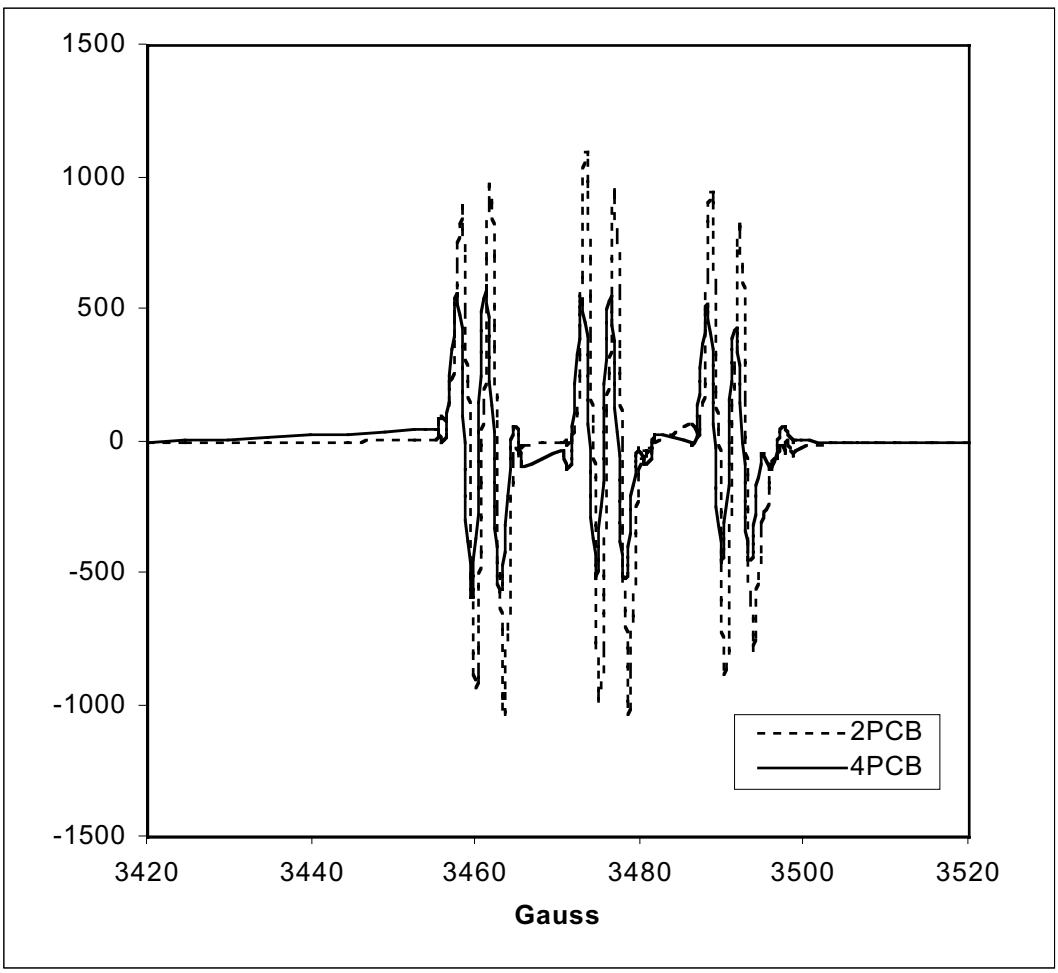

Fig. 2: First – derivative ESR spectrum of PBN-phenyl detected after 10 minutes of sonicating separate solutions of 2-PCB (4.6 mM) or 4-PCB (5.2 mM) at 20 kHz and 30.4 Wcm^{-2} in an Ar - saturated solution.

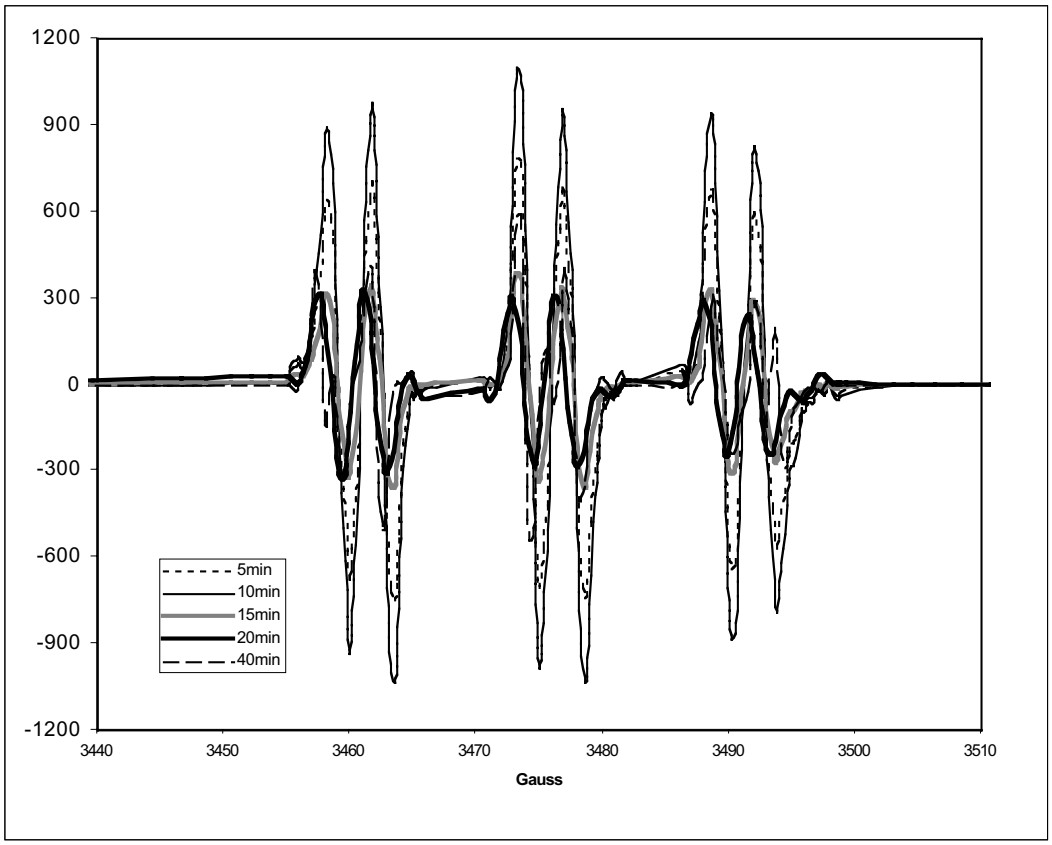

Fig. 3: First – derivative ESR spectrum indicating the accumulation of PBN-phenyl during sonication of 2-PCB (4.6 mM) at 20 kHz and 30.4 Wcm^{-2} in an Ar saturated solution. A maximum peak area occurs after 10 minutes of sonication.

concentration of the parent compound, 2-PCB, has decreased, and therefore, the rate of formation of phenyl radical decreases. Also, the spin-adduct itself further reacts during sonolysis. The formation of phenyl radical confirms thermolytic cleavage of the biphenyl rings, which is a key step in PCB destruction. Additional reactions yield other by-products, which were identifiable by Gas Chromatography – Mass Spectroscopy (GC-MS).

Three groups of products were identified with the mass spectra of sonicated PCB solutions. The first group includes biphenyl and toluene, ethyl benzene, diethylbiphenyl, and dibutenylbiphenyl. The second group includes phenol, propylphenol, di-*tert*-butylphenol, and cyclohexenyl di-phenol. Biphenyl was found only during the sonication of 54 mM 2-PCB, while others were detected as sonication products at lower initial concentration (5.2 mM) of 2-PCB. The third group consists of ethyl benzene, diethylbiphenyl, and trichlorophenol detected during the sonication of 2,4,5-PCB.

There are two possible pathways for formation of biphenyl. One is cleavage of C-Cl bond followed by H• addition:

$$C_{12}H_9Cl \rightarrow C_{12}H_9\bullet + Cl\bullet \tag{4}$$

$$C_{12}H_9\bullet + H\bullet \rightarrow C_{12}H_{10} \tag{5}$$

Another pathway is combination of two phenyl radicals:

$$C_{12}H_9Cl \rightarrow C_6H_5\bullet + C_6H_5Cl\bullet \tag{6}$$

$$C_6H_5\bullet + C_6H_5\bullet \rightarrow C_{12}H_{10} \tag{7}$$

Bond energies can be used to estimate activation energies. Therefore, because the bond energy for Cl-$C_{12}H_9$ is lower (397 $kJmol^{-1}$) than that of C_6H_5-C_6H_5Cl (418 $kJmol^{-1}$), dechlorination is expected to occur more rapidly than recombination of the biphenyl. The ESR data cannot be used to differentiate between these two pathways, however, because Cl• is difficult to detect directly by ESR, due to its high reactivity. The presence of methanol as a co-solvent contributes to the formation of CH_3• and •CH_2OH during sonication of 54 mM 2-PCB, but is unlikely to impact the formation of biphenyl.

The following pathways are proposed for the formation of other compounds in the first group. The thermal degradation of phenyl radical can produce C_6H_4•:

$$C_6H_5\bullet \rightarrow C_6H_4\bullet + H\bullet \tag{8}$$

Alkyl fragments result from rupture of the aromatic ring. β-scission of phenyl radical will yield n-C_4H_3• and acetylene:

$$C_6H_5\bullet \rightarrow HC{\equiv}C\text{-}CH{=}CH\text{-}CH{=}CH\bullet \tag{9}$$

$$HC{\equiv}C\text{-}CH{=}CH\text{-}CH{=}CH\bullet \rightarrow HC{\equiv}C\text{-}CH{=}CH\bullet + C_2H_2 \tag{10}$$

The acetylene then reacts with OH• to form methyl radicals and carbon monoxide:

$$C_2H_2 + OH\bullet \rightarrow CH_3\bullet + CO \tag{11}$$

The formation of group one compounds results from reactions between the phenyl radical and C_6H_5v, C_6H_4•, C_4H_3•, CH_3•, H• and C_2H_2. Group two compounds are formed by direct attack of group one compounds by •OH.

The third group of compounds (ethyl benzene, diethylbiphenyl, trichlorophenol) were detected during sonication of 2,4,5-PCB. Cleavage of the biphenyl ring yields a phenyl and a trichlorophenyl radical. Subsequent reaction of the phenyl radical with C_2H_2 will result in formation of ethyl benzene, and attack of the trichlorophenyl radical by •OH will yield trichlorophenol. The presence of hexane as a co-solvent can produce alkane free - radicals and may contribute to the formation of ethyl benzene and diethyl biphenyl. However, during soniction, C_2H_2 forms even in the absence of hexane. The wide range of organic by-products detected by GC/MS result from the reaction of aromatic free - radicals with other carbon centered radicals, or with hydroxyl radical (•OH). These experimental results confirm that free radical attack and thermolysis are major mechanisms in sonochemistry.

b. Sonication of 1,4–Dioxane

1,4–Dioxane is a volatile organic compound suspected of being a human carcinogen and is resistant to degradation by aerobic and anaerobic biological processes. This research focuses on the novel use of sonolysis in environmental pollution control applications. The objectives of this investigation are to 1) examine the kinetics and mechanisms of 1,4-dioxane degradation during sonolysis and 2) enhance the performance and efficiency of sonochemical technology. This current study considered the effects of various sparge gases (O_2, Ar, and air) at different sound frequencies for the degradation of 1,4-dioxane and examined the $OH^{\cdot}$ production of ultrasound in order to determine the optimal conditions for contaminant mitigation.

The degradation of 1,4-dioxane is also shown to be more efficient with a pure oxygen sparge than with pure Ar (Fig. 4). Although the thermal conductivity of O_2 is higher than that of Ar (48.1 vs. 30.6 mW/m-K), the production of additional radical species with O_2 can compensate for the lower internal cavitation temperature that arises with O_2. However, it is clear that a combination of the sparge gases O_2 and Ar lead to higher degradation rates than either pure gas, with the highest degradation rate occurring at a 75% Ar/25% O_2 ratio ($k = 4.10 \times 10^{-4}\ s^{-1}$).

With the 75% Ar/25% O_2 sparge ratio, there is an optimum balance created between the higher heat generated during acoustic cavitation from Ar and the generation of active radical species from O_2 which leads to the most effective conditions for compound destruction. The observed rate constant with a 75% Ar/ 25% O_2 sparge gas ratio is higher than that determined in the direct photolysis of 1,4-

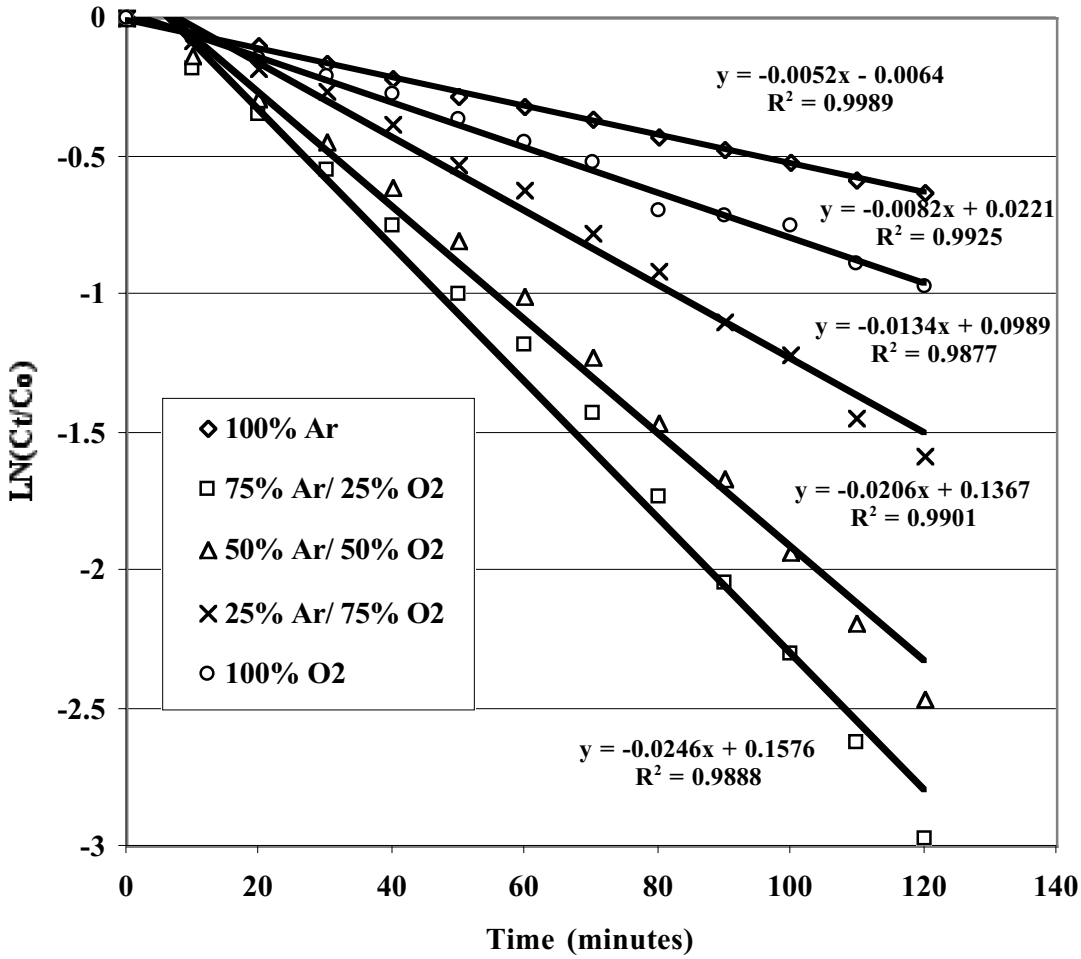

Figure 4: 1,4 - Dioxane degradation with various gas sparges. Frequency = 358 kHz and initial 1,4 – Dioxane concentration =Co = 1 mM. C_t = 1,4 – Dioxane concentration at time, t.

dioxane (k = 6.4 x 10^{-5} s^{-1}) but lower than the observed rate constant for the UV/H_2O_2 degradation of the same compound (8.7 x 10^{-3} s^{-1}).

The impact of frequency on sonolytic processes is significant. The results have varied widely due to the use of different types of ultrasonic emitters such as probes or plates and the diversity of reactors incorporated. The effect of sonolysis on the degradation rate of 1,4-dioxane was studied over a range of frequencies using the same transducer and reactor system for each experiment. The sparge gas ratio used was 75% Ar/25% O_2 and the results are shown in Figure 6. The fastest degradation rate occurs at a frequency of 358 kHz followed by 618, 1071, and 205 kHz.

The effect of sparging with air instead of argon or oxygen at different ultrasonic frequencies was considered and the results are show in Figure 6. Air has a thermal conductivity of 45.7 mW/m-K which is higher than Ar but lower than O_2. The rate constants observed in solutions saturated with pure air, Ar, and O_2 at 358 kHz are 1.23 x 10^{-4}, 8.67 x 10^{-5}, and 1.37 x 10^{-4} s^{-1}, respectively. The observed trends with air sparging are very similar to that of the 75% Ar/25% O_2 sparge with the two best degradation rates occurring at 358 kHz and 618 kHz. The kinetic rates, however, are lower by a factor of three in the air sparged solutions at each corresponding frequency when compared to the optimal combined Ar/O_2 sparge.

A number of experiments need to be performed in order to fully understand the mechanisms of 1,4-dioxane degradation. A thorough analysis of 1,4-dioxane byproducts will be evaluated using various analytical instruments.

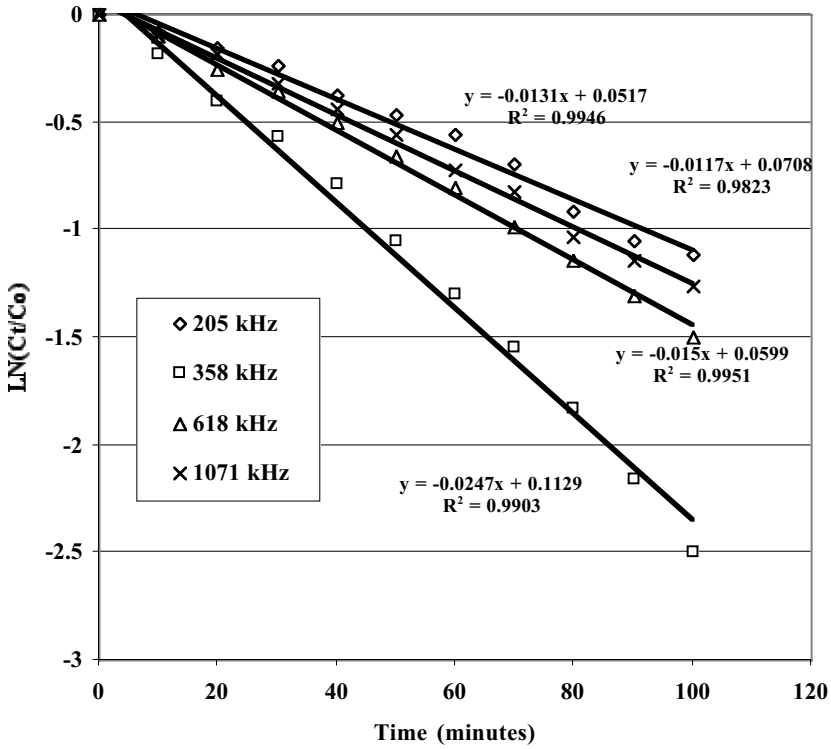

Figure 5: 1,4 dioxane degradation at four ultrasonic frequencies using the glass reactor : sparge gas = 75% Ar/25% O_2. C_t = 1,4 – Dioxane concentration at time, t, and Co = initial 1,4 – Dioxane concentration.

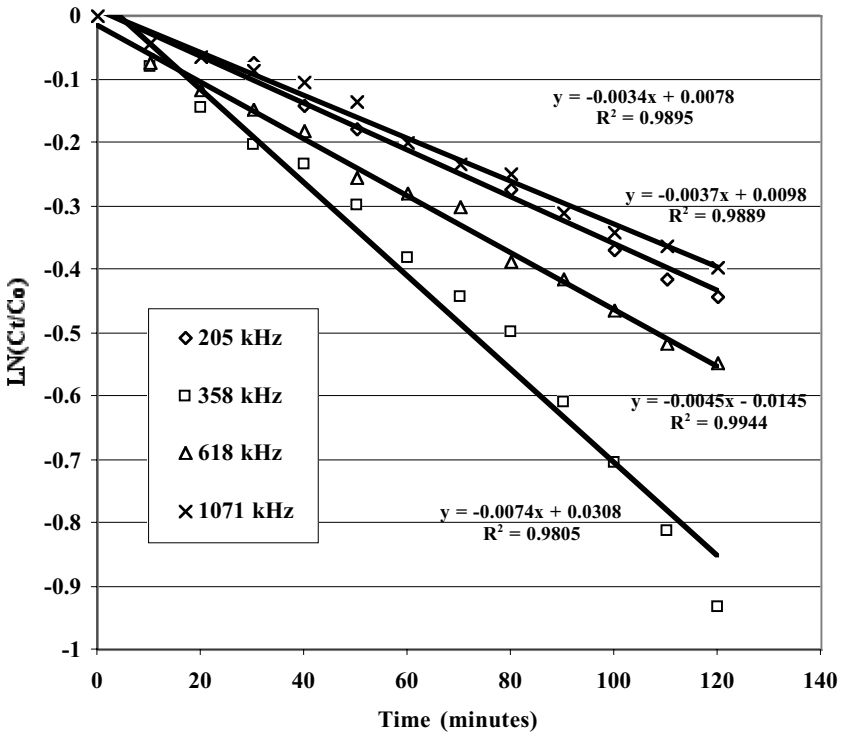

Figure 6: 1,4 Dioxane degradation at four ultrasonic frequencies using the glass reactor: sparge gas = 100% air. C_t = 1,4 – Dioxane concentration at time, t, and Co = initial 1,4 – Dioxane concentration.

c. Impact of Solid Particles on Sonolytic Destruction of Halogenated Hydrocarbons

Most investigations of sonochemistry for the purposes of water pollution control are performed with reagent grade water, which does not closely mimic environmental matrices. Natural waters and most industrial process streams contain solid impurities. Therefore, it is necessary to assess the viability of sonication in heterogeneous systems.

Previous investigations of heterogeneous sonochemistry have involved ultrasonic extraction of pollutants from sediments and ultrasound assisted reactions employing solid catalysts. However, more extensive quantitative results are needed concerning sonochemistry in environmentally relevant systems. We report results of a preliminary set of experiments, involving the ultrasonic irradiation of bromobenzene, trichloroacetonitrile, and chloropicrin in the presence of silica solids (15 mm and 10 nm).

The data in Fig. 7 demonstrate that in the presence of 15 micron solid particles, there is a slight or moderate impact on destruction kinetics. The destruction rate constant of trichloroacetonitrile (TCA) decreases by approximately 10% when the silica particle concentration is increased from 0 to 100 g L^{-1}. In the presence of 10 nm silica (Fig. 8), the trends are similar, with slight to moderate decreases in the reaction rate constant as the silica particle concentration increases.

In addition to adsorption, a number of other physical processes can occur in the presence of particles during sonication. For example, particles may serve as nucleation sites for cavitation bubbles. Further experimental work is required in order to adequately interpret these results.

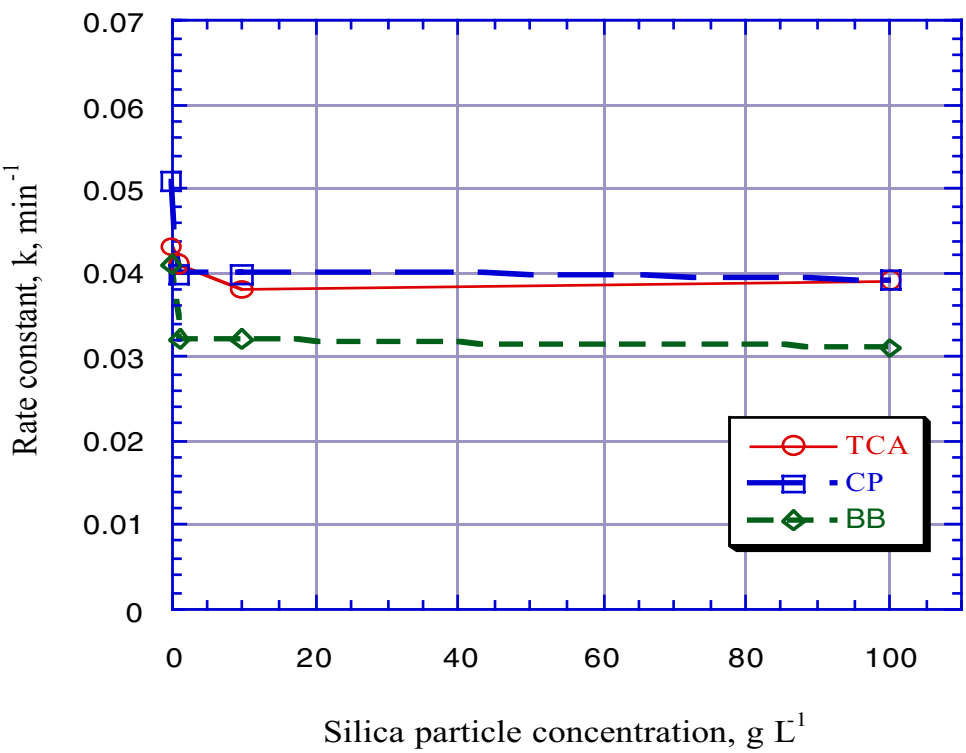

Figure 7: Sonication of trichloroacetonitrile (TCA), chloropicrin (CP), and bromobenzene (BB) in air-saturated solutions and intensity = 30.8 W cm^{-2}. 15 micron silica particles were employed.

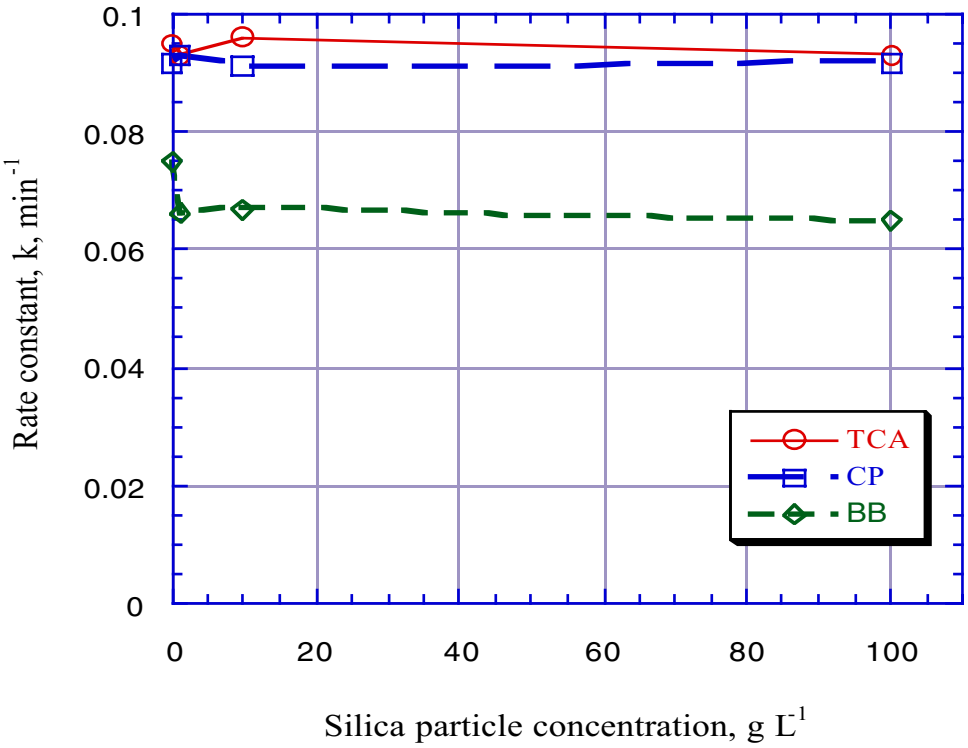

Figure 8: Sonication of trichloroacetonitrile (TCA), chloropicrin (CP), and bromobenzene (BB) in air-saturated solutions and intensity = 66.2 W cm^{-2}. 10 nm silica particles were employed.

Planned Activities

Further investigations of chemical kinetics and transformation products will be carried out during the final phase of the project. In order to truly understand sonochemical effects, the behavior of the individual bubbles and the bubble clouds must be more finely resolved. Physical characterization of cavitation bubble clouds will also be performed. Thus, a more fundamental link will be established between bulk, observable parameters and sonochemistry, via the physics and hydrodynamics of the cavitating cloud.

Publications Resulting from This Work

Pfalzer, U. and Hua, I.; **Ultrasonic Irradiation of Carbofuran: Decomposition Kinetics and Reactor Characterization,** *submitted,* October, 1998 to *Journal American Water Works Association.*

Zhang, G. and Hua, I.; **Cavitation Chemistry of Polychlorinated Biphenyls: Detection of Reactive Intermediates and By-Products and the Impact of Ultrasonic Frequency,** *submitted*, October, 1998 to *Environmental Science and Technology.*

Schramm, J. and Hua, I.; **Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism and Mass Balances,** *submitted, November, 1998, to Environmental Science and Technology.*

Conference Presentations Resulting from This Work

"Degradation of Dichlorvos by Sonolysis", Jennifer Schramm and Inez Hua at American Chemical Society Meeting; September, 1997, Las Vegas, NV.

"Sonochemical Degradation of Carbofuran in a Parallel-Plate Near-Field Acoustical Processor", Ulrike Pfalzer and Inez Hua, 20th Annual Midwest Environmental Chemistry Workshop, November 9, 1997, Indiana University, Bloomington, IN.

"Destruction of Polychlorinated Biphenyls in Acoustically Cavitating Systems", Guangming Zhang and Inez Hua, at American Chemical Society Meeting, March 1998, Dallas, TX.

Inez Hua,"The Use of Ultrasonic Irradiation in Environmental Engineering Processes", at Borchardt Conference, February, 1999, The University of Michigan, Ann Arbor, Michigan.

Other Access To Information

Hua, I., Höchemer, R.H., Hoffmann, M. R., **Sonolytic Hydrolysis of *p*-Nitrophenlyacetate: The Role of Supercritical Water,** *Journal of Physical Chemistry*, 1995, 99(8), pp. 2335-2342.

Hua, I., Höchemer, R.H., Hoffmann, M. R., **The Sonochemical Degradation of *p*-Nitrophenol in a Parallel-Plate Near-Field Acoustical Processor,** *Environmental Science and Technology*, 1995, 29(11), pp. 2790-2796.

Hua, I., Hoffmann, M. R., **Kinetics and Mechanism of the Sonolytic Degradation of CCl_4: Intermediates and By-Products,** *Environmental Science and Technology*, 1996, 30(3), pp. 864-871.

Hoffmann, M. R.; Hua, I.; Hoechemer, R., **Application of Ultrasonic Irradiation for the Degradation of Chemical Contaminants in Water,** *Ultrasonics Sonochemistry,* 3(3), pp. S163-S172, 1996.

Weavers, L. K., Hua, I., Hoffmann, M. R., **A New Advanced Oxidation Process: Photoassisted Oxidation of Triethanolamine by Periodate,** *Water Environment Research*, 69(6), pp. 1112-1119, 1997.

Hua, I., Hoffmann, M. R., **Sonochemical Production of Hydroxyl Radical and Hydrogen Peroxide: The Effect of Frequency and Saturating Gas,** *Environmental Science and Technology,* 31(8), pp. 2237-2243, 1997.

Hoffmann, M. R., Hua, I., Höchemer, R. H., Willberg, D., Lang, P., Kratel, A., chapter entitled **"Chemistry under Extreme Conditions in Water Induced by Electrohydraulic Cavitation and Pulsed-Plasma Discharges",** in *Chemistry Under Extreme or Non-Classcial Conditions*, pp. 429-478, edited by R. Van Eldik and C. D. Hubbards, New York: Wiley ; Heidelberg : Spektrum, 1997.

Professor Hua's Web URL is: http://CE.www.ecn.purdue.edu/CE/Fac_Staff/Env_Hyd/hua

Fundamental Studies of the Removal of Contaminants from Ground and Waste Waters via Reduction by Zero-Valent Metals

Project ID: 55061

Jory A. Yarmoff, University of California

Christopher Amrhein, University of California

Research Objective

Oxyanions of uranium, selenium, chromium, arsenic, technetium, and chlorine (as perchlorate) are frequently found as contaminants on many DOE sites. A potential remediation method is to react the contaminated water with zero-valent iron (ZVI). In this reaction, the iron serves as both an electron source and as a catalyst. Elemental iron is already being used on an experimental basis at many sites. Both *in situ* reactive barriers and above-ground reactors are being developed and field tested at this time. However, the design and operation of these treatment systems requires a detailed process-level understanding of the interactions between the contaminants and the iron surfaces. We are performing fundamental investigations of the interactions of the relevant compounds with Fe filings and single- and poly-crystalline surfaces. The aim of this work is to develop the fundamental physical and chemical understanding that is necessary for the development of cleanup techniques and procedures.

Research Progress and Implications

As of February 2000, we have performed bulk chemical measurements of the reduction reactions and surface science studies of model chemical systems. We have focused primarily on the reactions of uranyl, selenate, and arsenic with elemental iron. We also worked with chromate, perchlorate, and carbon tetrachloride. Our studies have led to a new understanding of the surface adsorption and precipitation of these contaminants in reactive-barrier walls.

A. Bulk chemical studies

We studied the reactions of various oxyanions with ZVI to determine the optimum conditions for remediation. We characterized the effects of pH, O_2 concentration, ionic strength and solution composition, degree of agitation, and iron surface pretreatment on the removal of UO_2^{2+}, $As(OH)_3^o$, AsO_4^{3-} SeO_4^{2-}, CrO_4^{2-}, ClO_4^-, NO_3^-, and CCl_4 in synthetic and natural groundwater solutions. Overall, the kinetics of trace element reactions with ZVI were dramatically different than expected. In the absence of O_2, the reduction and removal of trace elements was first-order with respect to both contaminant concentration and the ratio of the iron surface area to solution volume. Increases in the pH, ionic strength, or bicarbonate concentration decreased the rate of reduction, with pH being the most important variable. Under aerobic conditions, the reduction rate was 2 to 3 times faster but rapidly decreased due to passivation by iron oxyhydroxide precipitates. In the presence of oxygen, all the reactions were accelerated. However, the formation of Fe(III) oxyhydroxide precipitates led to passivation of the iron and, in the field, barrier plugging has been observed. Reactions without oxygen were slower, but long-term performance of the ZVI was improved in many cases. Thus, additives that help to deplete oxygen from groundwater prior to a reactive barrier need to be further investigated. The fact that the reduction reaction was faster at high electrode potentials indicates that oxidation of the iron, and not the reduction of the contaminant, is the rate-limiting step. A palladium

coating on the iron metal tripled the rate of trace element reduction. However, there was no reduction of perchlorate by either iron or Pd-coated iron.

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy of the reacted iron was carried out at the Stanford Synchrotron Radiation Laboratory (SSRL). One of the more interesting results was that As(V) (arsenate) was not reduced to As(III). There was some concern that the more toxic and mobile form of arsenic, As(III), might form in a reactive barrier wall. This unexpected result expands the applicability of ZVI reactive barrier walls. NEXAFS analysis of the iron and corrosion products from the selenate reactions showed mixtures of elemental Se and selenite, Se(IV). Studies carried out with chromate revealed that it passivated the surface of the iron and this passivation slowed down the sorption and reduction of other trace elements. X-ray diffraction (XRD) was used to determine the species of iron oxyhydroxides formed as a result of reaction with ZVI. The dominant product was lepidocrocite (γ-FeOOH) with minor amounts of maghemite (γ-Fe_2O_3) and "green rust".

Long term studies are ongoing to determine the potential for resolubilization of uranium from the ZVI surface. Solutions of varying ionic strength, pH, alkalinity, pCO_2, and pO_2 were reacted with ZVI for 6 months to determine if the precipitated uranium can be redissolved, after all of the material has been oxidized. Initial results have shown that a small "pulse" of U goes into solution when the solutions are switched from anaerobic to aerobic conditions. However, the amount of U resolubilized was <3% of the total precipitated U. These findings suggest that the long-term immobilization of U by ZVI does occur and permanent emplacement of iron reactive barrier walls is feasible.

B. Surface studies of reactions in aqueous solution

The evolution of the surface morphology during reaction in aqueous solution was investigated with scanning tunneling microscopy (STM). An *in situ* STM method, which continuously monitored the same spot as the reaction proceeded, showed that Fe surfaces are smoothed by reaction. The chemical composition and oxidation states of the surface products were measured with x-ray photoelectron spectroscopy (XPS). It was found that selenate deposits onto Fe surfaces by reduction to Se(IV). The amount of Se deposited is slightly increased if the atmospheric gases are removed by N_2 purging. This is attributed to a thickening of the Fe oxide layer when O_2 is in solution. We obtained the same basic results for the removal of chromate. Uranium, however, was deposited as U(VI), i.e., it was not reduced. It has generally been assumed that zero-valent iron removes contaminants from solution by a surface redox process, but these results indicate that this is not the mechanism operative for uranium removal.

The removal of uranium had an additional surprising result. When the dissolved atmospheric gases were removed, an extremely thick film (~1 μm) of uranium oxide was deposited. Note that because of the uniqueness of these films, we have had requests from research groups in the U.S. and in Europe for samples to be used in other experiments. A number of measurements were used to characterize the films. Scanning electron microscopy (SEM) indicated that the surfaces are fairly smooth, but contain microscopic cracks. X-ray diffraction (XRD) did not show any peaks, suggesting that the films are amorphous. Rutherford backscattering spectroscopy (RBS) showed that the film is composed of UO_3 with water incorporated. If the atmospheric gases remain in solution, only a thin film (12 Å) is formed. This difference is likely due to the presence of aqueous CO_2, which reacts with uranium to form uranyl-carbonate complexes. Thus, dissolved CO_2 and bicarbonate play important roles in determining the amount of uranium that can be effectively removed by ZVI. Since anaerobic conditions are beneficial in minimizing Fe-oxyhydroxide formation, it might be desirable to modify the chemistry of the groundwater prior to reaction with iron. However, the use of organic matter to remove oxygen will greatly increase the CO_2 concentration. Further work is being conducted to determine the effects of pH, uranium concentration, alkalinity, and ionic strength on the film growth.

C. Surface studies of model reduction systems

In order to probe the reduction reaction mechanisms on an atomic scale, we have investigated reactions of model gas-phase molecules with atomically clean iron in ultra-high vacuum (UHV). We began with the reaction of SeF_6 with iron and iron oxide surfaces, since Se in SeF_6 is in the +6 oxidation state just as in selenate, and SeF_6 is easy to employ in vacuum. We prepared atomically clean

polycrystalline Fe foils, and Fe foils with controlled coverages of oxygen. We exposed the surfaces to SeF_6, and used XPS to monitor the coverage and oxidation states of the adsorbed Se and the changes to the chemical states of the Fe surfaces. We found that the major reaction pathway involves the reduction of Se by complete dissociative adsorption. In the presence of minute amounts of adsorbed oxygen, the reaction of SeF_6 is dramatically suppressed. These fundamental surface chemical studies show that the reduction process itself is inherent to surface reactions with iron metal, and that the reaction is severely perturbed by the presence of oxygen.

Planned Activities

The bulk and surface studies described above will be continued employing different materials. For example, we will use Fe single crystals for reaction of SeF_6 in order to obtain detailed information on the adsorption sites. We will also perform similar measurements for the adsorption of UF_6, and for other volatile oxyanion reactants that can be reduced by iron, such as selenic acid and various chlorohydrocarbons. New work to be done involves having better control of the starting surfaces. We have completed the design of a unique wet cell that allows samples to be prepared with UHV techniques, and to then be reacted under solution without any exposure to the atmosphere. In this way, we can probe the reaction with absolutely clean Fe, or with Fe covered with controlled amounts of oxide, hydroxide or a metal coating. This wet cell is attached to our XPS/STM chamber so that we can immediately analyze the reacted surfaces. Samples of ZVI from a reactor at Rocky Flats have been obtained and we are preparing to analyze them for total U content and oxidation state distribution using NEXAFS. We have beam time scheduled at the SSRL for April 26-30, 2000 for these measurements.

Information Access

1. A.S. Mutziger, "Factors affecting the reductive dechlorination of carbon tetrachloride by zero-valent iron" (M.S. Thesis, University of California, Riverside, 1997).
2. M.J. Roberson, M.L. Hunt, C. Amrhein, S.R. Qiu, and J.A. Yarmoff, "Removal of selenate from irrigation drainage water using zero-valent iron", Environ. Sci. Technol., returned for revision.
3. S.R. Qiu, H.-F. Lai, M.J. Roberson, M.L. Hunt, C. Amrhein, L.C. Giancarlo, G.W. Flynn and J.A. Yarmoff, "The removal of contaminants from aqueous solution by reaction with iron surfaces", Langmuir **16**, 2230 (2000).
4. S.R. Qiu, H.-F. Lai, and J.A. Yarmoff, "Self-limiting growth of metal fluoride thin films by oxidation reactions employing molecular precursors", Phys. Rev. Lett., submitted.
5. S.R. Qiu, H.-F. Lai, H.T. Than, C. Amrhein, and J.A. Yarmoff, "Reaction of SeF_6 with iron and iron oxide surfaces: A model system for the study of selenate reduction", in preparation.
6. S.R. Qiu, M.L. Hunt, C. Amrhein, R. Pfeffer, T.E. Madey and J.A. Yarmoff, "The characteristics of uranium oxide films grown by surface adsorption at solid-liquid interfaces", in preparation.
7. M.L. Hunt, "Redox reactions and precipitation products of As(III) and As(V) on zero-valent iron" (M.S. Thesis, University of California, Riverside, 1999).
8. M.J. Roberson. "Removal of selenate from irrigation drainage water using zero-valent iron" (Ph.D. Dissertation, University of California, Riverside, 1999).
9. M.J. Roberson, C. Amrhein, and M. Hunt, "X-ray absorption near edge spectroscopy for the identification of selenium species on zero-valent iron" Presented at the 16th World Congress of Soil Science. Paper published on CD-ROM in Symposium 6, Paper #1942. pp. 1-3, (1998).
10. C. Amrhein, M.J. Roberson, M.L. Hunt, S.R. Qiu, and J.A. Yarmoff, "Oxyanion adsorption and reduction on zero-valent iron and iron oxides", Agronomy Abstracts, p. 207 (1999).
11. M.L. Hunt, B.A. Manning, S.R. Qiu, M.J. Roberson, J.A. Yarmoff, and C. Amrhein, "Sorption and oxidation of arsenic (III) on zero-valent iron", Agronomy Abstracts, p. 214 (1999).
12. C. Amrhein, M.L. Hunt, M.J. Roberson, J.A. Yarmoff, and S.R. Qiu, "The use of XANES, STM, and XPS to identify the precipitation products formed during the reaction of U, Cr, and Se with zero-valent iron", V.M. Goldschmidt Conference Extended Abstracts, Mineralogical Mag. 62A:51-52 (1998).

Phase Equilibria Modification by Electric Fields

Project ID: 55119

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David W. DePaoli, Oak Ridge National Laboratory
Junhang Dong, Oak Ridge National Laboratory
Sotira Z. Yiacoumi, Georgia Institute of Technology

Research Objective

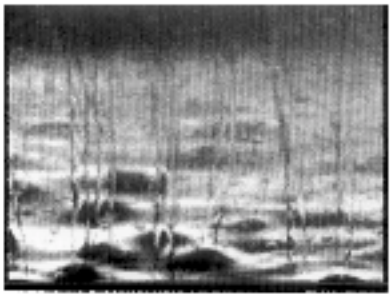
The objective of this project is to use electric fields to favorably manipulate the thermodynamic and transport properties of mixtures so that higher separation efficiencies can be achieved. The main focus is to understand and quantify the influence of electric fields on vapor-liquid, liquid-liquid, and solid-liquid systems. This program will lead to greater separation efficiency in a wide range of environmental treatment processes, including solvent extraction, sorption, distillation, and stripping. Such processes are widely used by DOE for treatment of wastes and sites contaminated with heavy metals, radionuclides, and organic solvents. Particular examples of applications of vapor-liquid-equilibria modification can be found in the separation of volatile organic compounds by either stripping or distillation. Improvements can also be made in liquid-liquid-extraction processes of TRU, Sr, Tc, and Cs by both thermodynamic and transport enhancements. Separations of metal ions by electrosorption can be used to remove such metal ions as Cs, Sr, Co, Pu, Cr, Cd, and Hg.

Research Progress and Implications

Following is a summary of the work after 2 and 2/3 years of a 3-year project:

Vapor-Liquid Equilibria: Experimental studies of electric-field effects on vapor-liquid equilibria have been completed and the results have been summarized in two peer-reviewed papers (Blankenship et al., 1999a and b) and a Masters thesis (Blankenship, 1999). It has been found that an electric field can be used to alter the vapor-liquid concentration of a binary mixture that involves at least one polar component. The mechanism has been investigated by Raman and FTIR spectroscopy. It was concluded that concentration changes in the vapor phase are caused by charge accumulation on the interface. In addition, transport effects of electric fields in distillation have been examined. It was found that electric fields can be used in distillation columns to decrease the bubble diameter and enhance mass transport rates.

Liquid-Liquid Studies: A new phenomenon of "tornado" formation at a liquid-liquid interface under electric fields has been uncovered. The figure below shows a typical image of liquid tornadoes rising from the toluene/isopropanol/water interface under an electric field applied across the interface. Tornadoes are formed, grow in diameter and height, and then become unstable forming droplets. However, the total population of the tornadoes is relatively stable when the operating conditions are well maintained. The population, intensity and size distribution of the tornadoes have been found to depend on the strength of the electric field, physical properties of the LL system, and the geometry of the experimental apparatus. *(More on liquid-liquid studies are described in the Optional Proprietary Information section).*



Tornadoes formed at the interface of toluene/isopropanol/water under an electric field.

Solid-Liquid Equilibria: Solid-liquid equilibria studies under electric fields have been conducted in an electrosorption apparatus, where the metal ion concentration in an aqueous solution was monitored as a function of an applied electric field between two parallel electrodes made of carbon aerogel. Unlike ion exchange, no additional chemicals are required for regeneration of the electrosorbent carbon aerogel in the system. Experiments were conducted to investigate the effects of solution concentration, electric field strength, and type of anion on electrosorption equilibrium. It was found that the mechanism of electrosorption is mainly based upon the electrical double layer formed on the electrode surfaces. Both the zeta potential of the electrode surface and the valence of removed ions influence the electrosorption capacity of the electrodes. A mechanistic model has been developed, incorporating both chemisorption and electrosorption, to predict the sorption capacity of electrodes as a function of the controlling parameters, including electrical potential and metal ion concentration. The overlapping effect of the electrical double layer is also considered because such an effect is inevitable in the pores of the carbon aerogel material, because of their broad pore size distribution. To demonstrate the importance of pore size on the removal of ions using electrosorption, the pore size distribution of carbon aerogel is incorporated in the modeling of the electrical double layer.

Planned Activities

A no-cost extension has been requested to complete this project by March 31, 2000. The following activities are planned for the remaining time: (i) Experiments will be conducted to investigate the effect of electric fields and phase inversion on mass transfer. (ii) Modeling studies of electrosorption will be completed. The following articles are in preparation to be submitted for publication in peer-review journals.

Phase Inversion of Liquid-Liquid Dispersions in the Presence of Electric Fields
Tornado Formation at a Liquid-Liquid Interface Due to an Electric Field
Electrosorption of Metal Ions from Aqueous Solutions
Distillation in the Presence of Electric Fields

Information Access

Shin, W-.T., S. Yiacoumi, and C. Tsouris, "Experiments on Electrostatic Dispersion of Air in Water," Industrial and Engineering Chemistry Research, **36**, 3647-3655 (1997).

Norato, M.A., C. Tsouris, and L.L. Tavlarides, "Phase Inversion Studies in Liquid-Liquid Dispersions," The Canadian Journal of Chemical Engineers, **76**, 486-494 (1998).

Tsouris, C., W.-T. Shin, and S. Yiacoumi " Pumping, Spraying, and Mixing of Fluids by Electric Fields," The Canadian Journal of Chemical Engineers, **76**, 589-599 (1998).

Blankenship, K.D., D.W. DePaoli, J.O. Hylton, and C. Tsouris "Effect of Electrode Configurations on Phase Equilibria with Electric Fields," Separation and Purification Technology, **15**, 283-294 (1999a).

Blankenship, K.D., V.M. Shah, and C. Tsouris "Distillation under Electric Fields," Separation Science and Technology, in press, 1999b.

Tsouris, C., A.P. Borole, and E.N. Kaufman, D.W. DePaoli "An Electrically Driven Gas-Liquid-Liquid Contactor for Bioreactor and Other Applications," Industrial and Engineering Chemistry Research, **38**, 1877-1883 (1999).

Tsouris, C., D.W. DePaoli, J.T. Shor, M.Z.-C. Hu, and T.-Y. Ying, "Electrocoagulation for Magnetic Seeding of Colloidal Particles," submitted for publication in Colloids and Surfaces, September 1998.

Tsouris, C., and J. Dong, "Effects of Electric Fields on Phase Inversion of Liquid-Liquid Dispersions," submitted for publication in Chemical Engineering Science, March 1999.

Tsouris, C., W.-T. Shin, S. Yiacoumi, and D.W. DePaoli, "Effects of Electric Fields on Bubble and Particle Velocities in Water and Alcohols," submitted for publication in Journal of Colloid and Interface Science, May 1999.

Blankenship, K.D., "Distillation with Applied Electric Fields," Master Thesis, Department of Chemical Engineering, University of Tennessee, April 1999.

Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

Project ID: 70135

Dr. Markus Flury, Washington State University

Research Objectives

Radioactive and hazardous waste stored in the underground tanks at the Hanford site has leaked or is suspected to have leaked into the vadose zone. Radionuclides, which are normally considered to be strongly sorbed (e.g., Pu and Cs), have been detected at much deeper depth than predicted based on current theories of vadose zone contaminant transport. There is strong indication that contaminants can be transported via colloids. Such colloid-facilitated transport is likely to occur at the Hanford site, where contaminants leaking from the storage tanks are released directly to the vadose zone. At Hanford, the potential for in situ formation of colloids as leaking tank waste enters the vadose zone is high. Tank waste supernatants are known to consist of solutions with high pH, ionic strength, and aluminate concentrations. When such alkaline solutions contact soils and sediments around the tanks, it is likely that soluble silica-rich allophane, feldspathoids, and zeolite-like materials are formed. These negatively-charged colloids are capable of adsorbing or coprecipitating with contaminant cations and moving through soil and sediment matrices. The objectives of this proposed project are to study three major processes responsible for colloid-facilitated transport: (1) formation and mobilization of colloids, (2) association of contaminants with colloidal particles, and (3) co-transport of colloids and contaminants in the vadose zone. We specifically consider chemical and geochemical conditions at the Hanford site. The radionuclide Cs is selected as a model contaminant. Soil or sediment samples representative of the porous material under waste storage tanks will be collected at the Hanford site. Formation of colloids will be studied in batch systems by reacting solutions typical for tank waste with vadose zone materials and with solutions expected at equilibrium with soil material. Colloids will be separated and characterized in terms of size, structure, composition, and surface charge characteristics. The interactions of Cs with colloidal particles isolated from the previous step will be investigated with batch sorption experiments and spectroscopic techniques. Transport and co-transport of colloids and the radionuclide Cs will then be studied with a series of laboratory column experiments using repacked Hanford sand material. Experiments will be carried out under unsaturated, steady-state as well as transient water flow to study the effect of water content on colloid transport. Magnetic Resonance Imaging will be used to visualize colloidal movement inside the porous medium. Sorption studies and column outflow data will be analyzed with numerical models to elucidate the relevant mechanisms responsible for contaminant sorption as well as colloid and radionuclide transport. Sorption and reaction models will be combined with transport models to quantitatively describe the column experiments. The results of the proposed research will lead to a better understanding of colloid-formation, colloid-contaminant-soil interactions, colloid migration, and colloid-facilitated transport in the vadose zone. The experiments proposed use conditions specific to the Hanford site, and the results are therefore directly applicable to clean-up strategies and procedures for Hanford contamination problems. We expect to provide conclusive evidence under what conditions, if any, colloid-facilitated transport can be expected at the Hanford site, and what the quantitative magnitude of this transport process will be.

Establishing a Quantitative Functional Relationship Between Capillary Pressure, Saturation and Interfacial Area

Project ID: 54793

Dr. Carlo D. Montemagno, Cornell University

Research Objectives

Through an integrated and focused research program that is comprised of theoretical, computational and experimental efforts this research effort is directed at: (1) improving on newly developed laboratory techniques to quantify and directly measure the functional relationship between phase interfacial area (a), saturation (S) and capillary pressure (Pc); (2) developing new computational algorithms in conjunction with laboratory measurements to predict Pc, S, and a; (3) testing exciting theory and developing new theory to describe the relationship between P{sub c}, S and a at the large scale; and (4) synthesizing the results of the experimental, computational and theoretical investigative efforts to develop a genetic model based upon an intrinsic soil metric to describe the functional dependence of Pc, S, and a. The results of this research could be used to generate a site specific soil moisture characteristic surface. Ultimately the results of this research could serve as the foundation upon which the true health and safety risk of site could be evaluated, the applicability of various remediation technologies examined, and the performance of implemented treatment strategies controlled.

Least-Cost Groundwater Remediation Design using Uncertain Hydrogeological Information

Project ID: 60069

George Pinder, University of Vermont

Summary

The research center for groundwater remediation design at the University of Vermont has been working for the last two years on a project that will provide a method of developing a groundwater remediation system that attains two objectives. This system will be a least cost design, and this design will avoid the risk associated with determining a system modeled using uncertain hydrogeologic information, namely the hydraulic conductivity of the contaminated aquifer.

The principal problem addressed in this research is the remediation of contaminated groundwater caused by the improper disposal of potentially harmful chemicals. Often these chemicals contaminate groundwater aquifers. The resulting contaminated groundwater may travel to surface water bodies, such as lakes or streams, where delicate ecosystems may be impacted, or it can reach domestic, municipal, or industrial wells thereby compromising their utility as a potable water supply.

The methods of optimization developed in this research and the techniques used to apply these methods can be applied to any risk-based optimization problem. This research explores methods of sampling distributions of uncertain parameters; it incorporates uncertainty into the optimization problem; and it utilizes a new solution technique to solve optimization problems where the objective function is nonconvex and cannot be expressed analytically. Many of the challenges addressed in this research are not unique to groundwater problems and consequently the DOE will be able to use the resulting methodology in many different computational problems.

The primary objective of this project is the development and evaluation of a new approach to the determination of a risk-based groundwater remediation system subject to gradient and concentration constraints. The proposed methodology will employ a groundwater flow and transport model to determine the location and pumping rates of groundwater wells. These wells will pump out contaminated water, treat it, and then replace it, possibly external to the modeled region of remediation. This is generally referred to as a pump and treat remediation design. The approach will work well in designing remediation systems when none are in place. It will also work as a way to improve the functionality or economy of an existing system.

The solution of the groundwater flow and transport model is dependent upon the assumed value of the hydraulic conductivity of the aquifer. The hydraulic conductivity of a groundwater aquifer, however, is uncertain. The degree of uncertainty of the hydraulic conductivity can be determined by examining spatially distributed values that are obtained from aquifer or laboratory tests. Using the results of these tests, a distribution of hydraulic conductivity is determined for a given aquifer. This distribution defines the risk involved in using a design determined from a single hydraulic conductivity value. If the distribution has a low variance, then the model has a low degree of risk. If the variance is large, however, the model has a high degree of risk.

Historically, risk has been addressed in optimization problems by using a stochastic approach to uncertain parameters appearing in an optimization problem. In the classical approach, bounds are placed on the admissible range of values of an uncertain parameter. Either the upper or the lower bound of the given parameter is then used to determine a less risky optimal solution. Using the stochastic approach results in an over determined system and does not take into account the frequency of occurrence of the lower- and upper-bound values. These values may only occur five percent of the time, and yet the model assumes these values have an equal probability of occurrence. When dealing with a least-cost design, this type of solution is not cost effective.

We apply a multiscenario approach to incorporate uncertainty in an optimization problem. In this method each scenario is a realization obtained using a different hydraulic conductivity field, the values of which are sampled from the hydraulic conductivity distribution function. The frequency of occurrence of each hydraulic conductivity value sampled from a given distribution is accounted for by using a method of optimization called robust optimization.

In robust optimization all scenarios are considered in the objective function of the optimization problem. One of the sampled scenarios is considered to be the true scenario while the other scenarios are considered in an additional term in the objective function called the penalty term. If a particular pumping scheme is implemented for these other scenarios and the constraints are violated in these scenarios, then the objective function increases. The value of the penalty associated with each scenario is equal to the total penalty weight value times an individual penalty weight times the actual penalty value of the constraint. The individual penalty weight is related to the frequency of occurrence of the particular scenario. If it is very important to avoid risk, then a large total penalty weight can be assigned for the given problem.

This research project focuses on two basic goals that can be achieved by a pump and treat remediation design. The first goal is to contain a plume of contaminated groundwater. The second is to manage risk through decreasing the concentration of contaminant in the groundwater at specified locations in the model. These goals are currently being addressed separately, but will be combined.

The containment problem does not involve contaminant transport. Therefore the fact that the hydraulic head response to pumping is linear is exploited. On the other hand, the objective function of the robust optimization problem for the containment problem is non-linear and nonconvex. In such a problem, the global minimum value occurs on the boundary of the feasible region. Outer approximation is a suitable method for solving this optimization problem.

The optimization problem that involves decreasing the concentration constraints at specified locations in the model is also nonconvex. However, the global optimum of this problem does not always occur on the boundary of the feasible region. Consequently a new method of solving nonconvex optimization problems of this nature, called the tunneling method, is being explored in this research to solve this problem.

The tunneling method determines the global-optimal solution of a given objective function by cycling through two phases. In the first phase, a local minimum is determined given a starting point. This minimization phase uses ordinary gradient search methods. The second phase is the tunneling phase. In this phase the original objective function is transformed into a tunneling function that has the property that a pole exits at the most recently determined local minimum. Further, roots of the tunneling function exist at points away from the pole where the objective function is equal to the value of the objective function at the most recently determined local minimum. Ordinary gradient methods are used to determine one such root of the tunneling function. Once a root is determined the location of the root is a new starting point for the next cycle of this method, i.e. the next minimization phase. The cycling of the tunneling method continues until no root exists for a given tunneling function. The tunneling method provides global-optimal solutions to optimization problems that are nonconvex, such as the groundwater remediation problem subject to concentration constraints.

We have successfully implemented the robust optimization problem for groundwater remediation problems subject to gradient constraints. We have also developed a method of sampling based upon Latin-Hypercube sampling that allows us to simplify the robust optimization problem by assigning a constant value for all individual penalty weights in the penalty term. This method of sampling is called equal area sampling. The area under the distribution curve between successively sampled points is equal to one over the total number of scenarios sampled plus one. This sampling technique not only allows us to use the same individual weight for all samples, but it also allows us to observe convergence of the robust optimization problem to a stable global optimal solution as the number of samples examined increases. By virtue of this investigation, the beta distribution has been found to be a better distribution function to use to describe the hydraulic conductivity than the more commonly used lognormal distribution.

We have also implemented the robust optimization problem for groundwater remediation problems subject to concentration constraints. The tunneling method has been successful at determining the global optimum for these problems. There is no analytic expression to describe how the objective

function changes with variable pumping schemes. Given a particular pumping scheme, the determination of the value of the objective function requires computing the solution to the groundwater flow and transport equations for each scenario sampled. Because of this computational intensity, the gradient methods employed in the tunneling method are time consuming.

In a study conducted on a very simple model where three equal area samples are considered in the Latin Hypercube approach, the tunneling method successfully determined a global optimum for the robust optimization problem. However, methods designed to make this method more efficient are being explored before the analysis of more scenarios is considered.

Planned Activities

The work that will be done during the remainder of this project will focus on optimizing the efficiency of the tunneling method and will continue with the completion of the study of the design of remediation systems subject to concentration constraints. Once this work is completed, the resulting methodology will be used to examine both gradient and concentration constraints. The tunneling method will be used to solve this problem.

Development of Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface

Project ID: 60158

Dr. Lewis Semprini, Oregon State University

Jonathan D. Istok, Oregon State University

Research Objective

The objective of this research is to develop a unique method for using naturally occurring radon-222 as an inexpensive partitioning tracer for locating and quantifying nonaqueous phase liquid (NAPL) contamination in the subsurface, and assessing the effectiveness of NAPL remediation. Laboratory, field, and modeling studies are being performed to evaluate this technique, and to develop methods for its successful implementation in practice.

Research Progress and Implications

This report summarizes work that has been accomplished after 1 1/2 years of a 3-year project. The research to date has included radon tracer tests in physical aquifer models (PAMs) and field studies at Site 300 of the Lawrence Livermore National Laboratory, CA, Site 100D at Hanford DOE Facility, WA, The Dover National Test Site, DE, and the Weyerhauser-Sycan Site, Beatty, OR.

During the past year PAM tests were completed that evaluated the ability of radon as a tracer to monitor TCE NAPL remediation by permanganate oxidation. The tests were performed in radial flow geometry to simulate the flow field during field push-pull tests used to evaluate the permanganate oxidation technology. The radon tests were easily incorporated into these experiments, since they simply rely on measuring the natural radon present in the pore fluid. Two types of radon tests were performed: 1) static tests, where radon was permitted to build-up to steady-state concentrations in the pore fluid before being measured, and 2) dynamic push-pull-tests, where the radon concentration response was monitored by injecting water that lacks radon into the PAM and pulling the water back and measuring radon concentration as a function of volume of water extracted. Both methods were found to be useful in monitoring the progress of NAPL remediation.

The PAM was packed with subsurface solids from LLNL Site 300, which emanated enough radon for its use as a natural tracer. Radon concentrations in 5-ml groundwater samples from the PAM were accurately measured using a low background Liquid Scintillation Method with Alpha-Beta-Discrimination Counting. Studies were performed with no NAPL present and then with the addition of 5 vol % TCE NAPL to a portion of the PAM. Repeated push-pull additions of high and low concentrations of permanganate were injected into the PAM during the course of the study and both static and dynamic radon tests were performed. The results of the static profiles are presented in Figure 1. Radon concentrations under static (no flow) conditions after TCE addition, but prior to permanganate treatment were a factor of two to three lower in the region that contained TCE. The reduction in radon concentration, however, was not as low as predicted by partitioning theory. Radon concentrations increased with successive injections of permanganate, and eventually reached levels that existed before TCE addition. The reason for the low radon level at sampling Port 1 is not known, but it may be associated with a build-up of carbon dioxide gas in this narrow region of the radial PAM. If a trapped gas phase is present, radon would partition into the gas phase and aqueous radon concentrations would be reduced. Overall the radon results indicated effective permaganate oxidation of the NAPL TCE. The results are consistent with observations of permanganate utilization, which

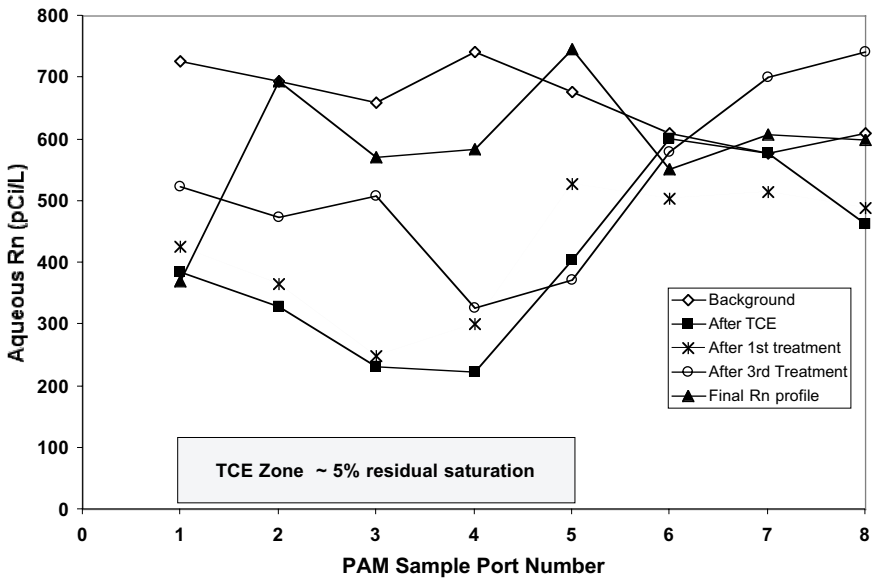


Figure 1. Static profiles of radon concentration in a PAM containing NAPL TCE that was remediated with successive addition of permanganate.

show extensive utilization when radon deficits were observed, and little permanganate utilization after the radon reached background levels.

Dynamic push-pull tests also show radon concentration responses changing as remediation proceeds. During the push (injection) phase water lacking radon was injected to probe the region that contained NAPL; during the injection phase flow was reversed and radon concentrations were measured in the extracted water. The results of these push-pull tests are presented in Figure 2.

The radon concentrations increased with successive treatments of permanganate, especially when the ratio of the extracted volume to injected volume was greater than 1.0. The results are consistent with those expected during the course of NAPL remediation. Consistent changes in the breakthrough patterns were not observed during these tests. This may result from dynamic changes in flow patterns, which were also indicated by concentrations of the bromide tracer. The results, however, do indicate that push-pull tracer tests utilizing radon have the potential for monitoring the progress of NAPL remediation. The results of these tests would indicate that the amount of fluid injected and extracted is an important consideration when using this method.

Currently we are determining the TCE remaining after treatment by measuring the TCE content in core samples. We are also measuring radon emanation from core samples to determine if changes occurred as a result of the remediation process.

Studies in a 2-D horizontal PAM (2 m x 4 m x 0.2 m) that is packed with aquifer solids from the Hanford Site were initiated. The PAM model is representative of aquifer conditions where regional flow can be induced. Initial static radon concentrations through the PAM have been determined and push-pull tests in wells surrounding the zone where NAPL is to be added have been completed. The results from the push-pull tests show very reproducible radon and bromide responses, with radon being transported similarly to the non-partitioning bromide tracer, as is expected with no NAPL present. Distributed TCE NAPL zones will now be created in the 2-D model and the static radon concentration distribution will be determined and push-pull tests will be repeated. TCE NAPL contamination will then be remediated using permanganate and the static and dynamic radon tests will be performed.

A field evaluation of the push-pull radon method was performed at the Weyerhaeuser-Sycan Site in Beatty, OR. Perchloroethene (PCE) NAPL contamination was suspected at a source zone of contamination. Push-pull studies were conducted along with permanganate injection experiments. Direct analysis of core samples for NAPL contamination was also performed. The push-pull tests showed similar radon and bromide breakthrough responses, indicating that NAPL was not present in

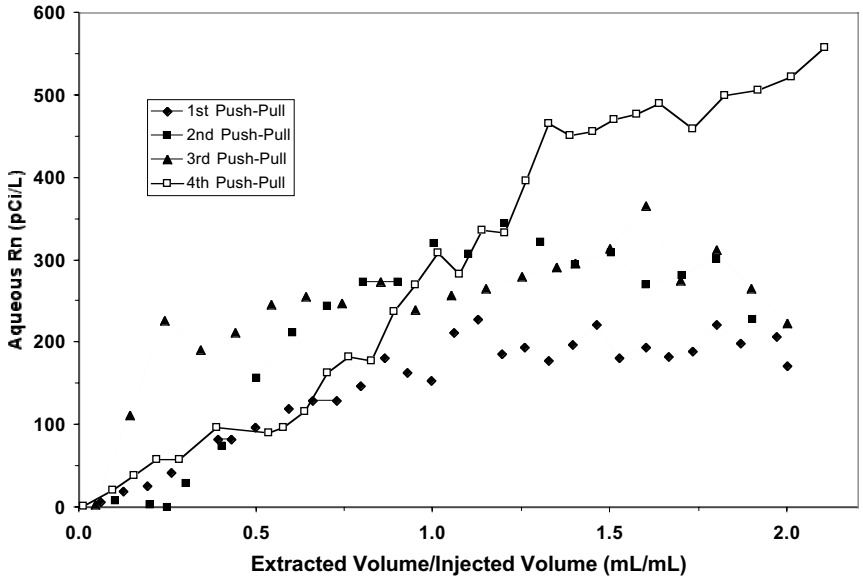


Figure 2. Radon concentrations as a function of ratio of the extracted to injected volume of a push-pull test.

the source zone. Little permanganate was utilized in the test zone, and core samples analysis show no detectable NAPL contamination, which are both consistent with the radon results.

A radon field survey was also performed of water from Test Cell 3 at the Dover National Test, DE. The test cell had been purposely contaminated with PCE. The radon survey was conducted under static flow conditions in the cell after no flow had occurred for a period of one month. Obtaining good groundwater samples from the test cell proved to be difficult due to plugging of sample points within the test cell. Many samples appeared to be stripped of both PCE and radon. In several locations samples were obtained that had low radon values and high PCE concentrations, which is expected if a NAPL zone was present. However, due to sampling problems that were encountered it is difficult to draw conclusions from these data. Over the past several months a study was performed of NAPL remediation using alcohol flushing methods. We are currently planning to monitor the radon concentrations in the cell to determine if changes occurred as a result of the flushing experiments.

Planned Activities

Studies in the 2-D horizontal PAM model will evaluate the radon response to NAPL remediation with permanganate. We also plan to construct a vertical PAM and perform radon studies in a layered system. We will investigate an industrial site that has NAPL contamination, using push-pull tests. We also will continue to investigate Test Cell 3, at the Dover National Test Site. Successive NAPL addition and remediation methods are planned in the test cell.

Information Access

Semprini,L., M. Cantaloub, S. Gottipati, O. Hopkins, and J. Istok. Radon-222 as a Natural Tracer for Quantifying and Monitoring NAPL Remediation in: *Nonaqueous-phase Liquids: Remediation of Chlorinated and Recalcitrant Compounds*, Eds:G.B. Wickramanayake and R.E. Hinchee, Battelle Press, Columbus, OH, 1998, pp. 137-142.

Semprini, L., O.S. Hopkins, and B.R. Tasker. "Laboratory, Field and Modeling Studies of Radon-222 as a Natural Tracer for Monitoring NAPL Contamination" Submitted to *Journal of Transport in Porous Media.*

Cantaloub, M., J.Istok, and L. Semprini "Investigations of Radon-222 as an Internal Tracer for Monitoring NAPL Remediation." *Symposium on Environmental Models and Experiments Envisioning Tomorrow; Behavior and Remediation of Nonaqueous Phase Liquid Contaminants in the Subsurface*, UC Irvine, CA July 20-23, 1998.

Semprini, L., J. Istok, and M. Cantaloub "Development of Rn-222 as a Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface" *Department of Energy Environmental Management Science Program Scientific Workshop*, Rosemont, IL July 27-30, 1998.

Cantaloub, M., J. Istok and L. Semprini "Site Assessment and Remediation Monitoring Using Naturally Occurring Rn-222" *The 5th International Petroleum Environmental Conference*, Albuquerque, NM October 20-23, 1998.

Cantaloub, M., J. Higginbotham, J. Istok and L. Semprini "Interaction of Sample, Cocktail and Headspace Volume when Measuring Aqueous Rn in Small Volume Samples." *44th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry*, Albuquerque, NM November 16-19, 1998

Cantaloub, M. "The Role of Cocktail Solvent on Radon Measurement by Liquid Scintillation Analysis." *Packard Instrument Co. Environmental LSC Workshop at the 44th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry*, Albuquerque, NM November 16-19, 1998.

Cantaloub, M., J. Istok and L. Semprini "Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface." *Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) Technical Symposium and Workshop*, Arlington, VA December 1-3, 1998.

Cantaloub, M., M. Humphrey, J. Istok and L. Semprini "Monitoring NAPL Remediation Using Rn-222 as an In-Situ Indicator." 1998 *Fall Meeting of the American Geophysical Union*, San Francisco, CA December 6-10, 1998.

Manipulating Subsurface Colloids to Enhance Cleanup of DOE Waste Sites

Project ID: 54888

Philip M. Gschwend, Massachusetts Institute of Technology

Carol R. Johnson, Massachusetts Institute of Technology
Nikolaos P. Nikolaidis, University of Connecticut
Lucas A. Hellerich, University of Connecticut

Research Objectives

Many DOE sites are polluted below ground with chemicals that cannot be readily pumped to the surface for treatment because those compounds associate too extensively with the immobile aquifer solids (Fig. 1a.) We are working to address this problem by using colloid mobilization to enable pumping the sorbents themselves out of contaminated subsurface sites (Fig. 1b.) To pump such colloidal sorbents out of contaminated subsurface sites, we must cause them to detach from the framework grains. Our experience indicates that this can often be done if the groundwater solution

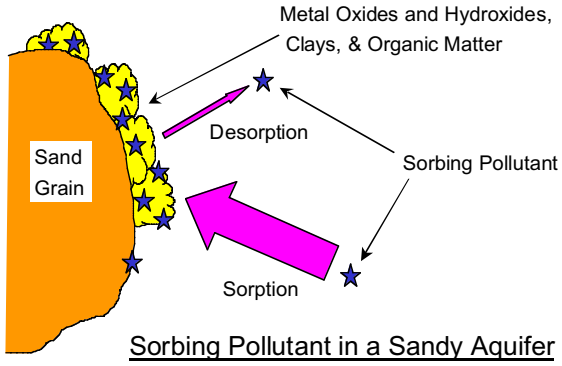


Figure 1a. Depiction of the situation when a pollutant (stars) has a strong tendency to sorb to metal oxyhydroxides, clays, and natural organic matter, rather than stay dissolved in groundwater. Pumping cannot effectively recover such compounds.

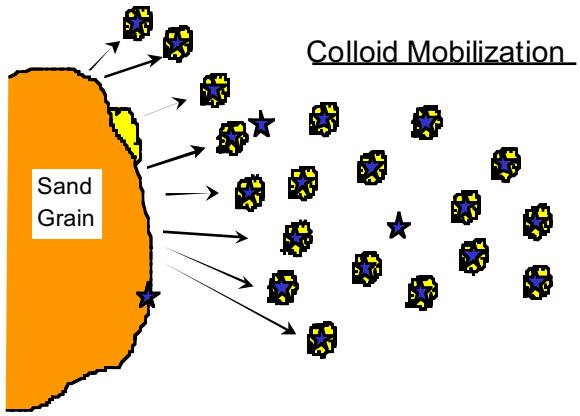


Figure 1b. Proposed situation after manipulating the groundwater composition so that colloids are mobilized, carrying pollutants of concern. Now pumping the groundwater will efficiently recover the compounds for treatment at the ground surface.

chemistry is suitably modified to (1) reverse the surface charges of key phases like amorphous iron oxyhydroxides, and (2) push the adjacent attached fines apart using electrostatic repulsions and expanded diffuse double layers.

This project sought to: (1) understand the forces which immobilize colloids in aquifers, (2) devise aqueous solutions which disrupt these forces, and (3) test the effectiveness of colloid mobilization as a technique for removing colloids from the aquifer.

Research Progress and Implications

We have demonstrated the feasibility of groundwater manipulations to cause colloid mobilizations at two field sites, Georgetown, SC (a clean coastal plain aquifer site with geology similar to DOE's Savannah River Site) and Putnam, CT (a glacial outwash aquifer that is heavily contaminated with chromium-plating wastes.) In these two cases, we characterized the subsurface mineralogy and geochemistry, proposed and tested specific sorbate amendments in the laboratory for their effectiveness at releasing colloids from the sites' solids, and then used a novel injection-withdrawal methodology to interrogate several positions at each of the two field sites for our ability to mobilize the colloids in the field. At both sites we achieved substantial success insofar as we could cause colloidal suspensions near 100 mg/L to be pumped from below ground (Fig. 2.) In addition, we found that designing

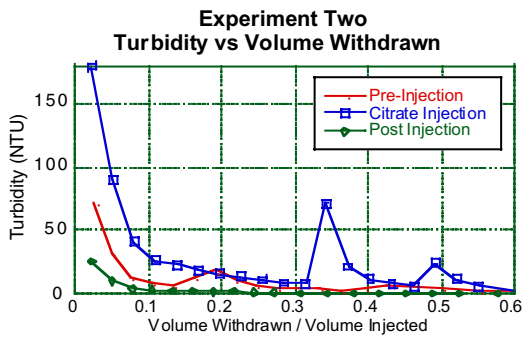


Figure. 2. Mobilization of colloids at the Cr-contaminated site in Connecticut using 5 mM citrate solution.

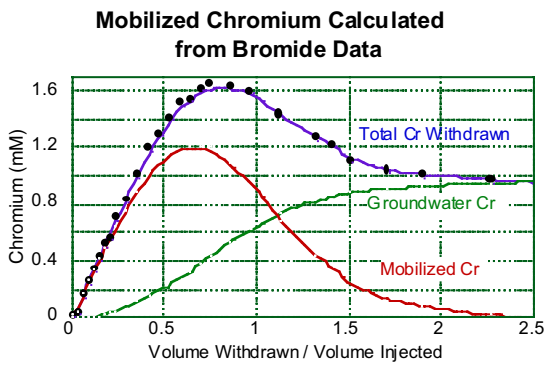


Figure 3. Recovery of chromium after injecting 5 mM citrate solution into Cr-contaminated site in Connecticut

injection solutions that optimally mobilize colloids in the field also promotes desorption processes. As an example, in manipulating chromium-containing colloids, we found that much of our injected sorbate also served to displace the ion exchangeable chromate load in that subsurface region (Fig. 3.)

Planned Activites

No further laboratory or field activities are planned as our funding has ended. We will continue to pursue publication of two papers, currently in preparation:

Hellerich, L.A., N.P. Nikolaidis, C.R. Johnson, and P.M. Gschwend. Bromide transport in a small-scale injection-withdrawal experiment.

Johnson, C.R., L.A. Hellerich, N.P. Nikolaidis, and P.M. Gschwend. Manipulating subsurface colloids by citrate addition to a chromium-contaminated aquifer.

The Dynamics of Vadose Zone Transport: A Field and Modeling Study Using the Vadose Zone Observatory

Project ID: 70149

Dr. Charles R. Carrigan, Lawrence Livermore National Laboratory

Research Objectives

A stated need of the DOE EM program is a better understanding of basic vadose zone fluid flow and contaminant transport processes for the purpose of making improved estimates of contaminant release rates and fluxes across the vadose zone to the water table at DOE sites such as the tank farms at Hanford. We propose to investigate details of the modes of contaminant transport with the aid of infiltration experiments designed to elucidate how vadose zone characteristics such as preferential pathways, heterogeneities, and relative permeabilities influence the transport of contamination in liquid, gas and colloidal phases to the water table. Beyond enhancing our basic understanding of vadose zone transport processes, this proposed effort would result in a vadose-zone-transport-characterization methodology that can be generalized to other DOE sites. To accomplish this, we will use the newly developed Vadose Zone Observatory (VZO) at Lawrence Livermore National Laboratory (LLNL) to carry out a partially subsidized, highly cost-effective study of multiphase fluid flow and colloidal transport in a heterogeneous unsaturated zone bearing dynamic resemblance to one type of Hanford vadose regime. The observatory consists of almost twenty instrumented boreholes and monitoring wells which traverse the 70-foot unsaturated zone including eight wells containing electric resistance tomography (ERT) arrays, four wells for electromagnetic induction tomography (EIT) and water table sampling, and four boreholes with multilevel gas-sampling ports, soil temperature sensors, gypsum blocks, tensiometers and lysimeters. The observatory uses several multichannel data loggers to continuously store information about surface barometric pressure, subsurface gas-phase pressure, subsurface temperature, capillarity and water-table levels that is downloaded into computers for later analysis. Using the capabilities of the VZO, we will continuously monitor the progress of an infiltration event simultaneously using both geophysical volumetric imaging techniques as well as more conventional hydrologic measurements (e.g., subsurface temperature, gas-phase pressure, tensiometry and lysimetry) that involve making observations at discrete points throughout the infiltration volume. An advantage of this approach is that volumetric imaging provides a context for interpreting the discrete observations, while discrete measurements provide a more detailed picture of changes in the vadose zone that cannot be obtained from the volumetric imaging observations themselves. Beyond this, the VZO permits samples of moisture and gases to be taken from many different depths in the vadose zone and from the water table. This ability to sample is critical to our infiltration experiments, which include a variety of chemical and isotopic gas- and liquid-phase tracers and colloidal particles. The release of chemical and isotopic tracers during infiltration events is an important feature of these proposed experiments since such tracers permit evaluation of the potentially complicated relationship between actual chemical transport and fluid flow in the unsaturated zone as determined by ERT or other imaging methods. With the goal of providing a comprehensive picture of multiphase vadose zone flow and transport, LLNL's NUFT (Non-isothermal Unsaturated Flow and Transport) computer program will be used to develop diagnostic models that serve as a framework for interpreting the wide variety of observations obtained during an infiltration experiment. With support from a hydrogeologist at Hanford, modeling will also provide the basis for applying our enhanced understanding of contaminant transport at the VZO to addressing transport issues at Hanford. Finally, by carrying out some infiltration experiments jointly with other LLNL principal investigators and a geophysical instrumentation company, we will leverage our effort as well as collaborate with them in developing improved subsurface imaging interpretations and technologies based upon the ERT and electromagnetic induction methods. In support of DOE educational programs, this proposal involves the participation of an MS-level student intern as well as a postdoctoral researcher.

Characterization of Contaminant Transport by Gravity, Capillarity and Barometric Pumping in Heterogeneous Vadose Regimes

Project ID: 54950

Dr. Charles R. Carrigan, Lawrence Livermore National Laboratory

Research Objectives

Many releases of chemical solvents or DNAPLS occur at the surface causing the vadose layer to be the first part of a hydrologic system to interact with the contaminant. As the entry point of these chemicals into a groundwater system, the vadose zone can become a long-term source function for contamination that is metered by natural processes into the underlying saturated zone for further dispersal. However, a contaminant plume does not remain unaffected by the surrounding unsaturated soil. Heterogeneous vadose regimes, such as those containing fractures or other permeability heterogeneities, are the sites of complex interactions between the atmosphere and groundwater. When a volatile contaminant exists as free product or in dissolved form in the vadose environment, upward transport can occur with the contaminant ultimately being vented as a vapor into the atmosphere. It is known that partitioning of a liquid contaminant into the vapor phase can be a very effective means of decontamination. The subsequent transport of the vapor occurs naturally and can be enhanced, for example, by the anisotropy resulting from fractured-matrix-flow paths as well as by certain heterogeneity distributions. Several stages in the transport process are involved in going from a volatile, liquid state contaminant to a contaminant vapor vented at the surface. In a three-year effort, we will investigate the detailed nature of each of these stages of transport in the vadose zones of fractured and heterogeneous regimes with the (1) aid of existing data, (2) new field studies involving dissolved tracer gases and (3) 3-D diagnostic computer simulations that provide a framework to interpret our observations. We will emphasize determining the impact of features specific to a site, that is, the local geology and hydrology, on each stage of the transport process. In particular we want to better understand how the time scales for (1) partitioning contaminants from the liquid to the vapor states and then (2) transporting the vapor out of the vadose regime are dependent on the specific character of a site. Such time-scale information will be important for determining the appropriate response to vadose zone contamination including the option of natural remediation, that is, no response. This information can also be interpreted as a baseline performance criterion for proposed soil-venting schemes. Not least, this work will result in the development of new field methods, involving the injection and analysis of dissolved rare-isotope and chemical-compound tracers, that we anticipate applying to sites at Lawrence Livermore and to the thick, fractured basalt vadose regime at the Idaho National Engineering Laboratory.

A Chaotic-Dynamical Conceptual Model to Describe Fluid Flow and Contaminant Transport in a Fractured Vadose Zone

Project ID: 55359

Dr. Boris Faybishenko, Lawrence Berkeley National Laboratory

Research Objectives

This research project was triggered by the investigation of a complex behavior of flow and transport in unsaturated fractured rocks at the INEEL contaminated sites. Preliminary investigations conducted at the Large Scale Infiltration Test in 1994 and the Box Canyon site in Idaho in 1995-1996, prior to the origination of this project, as well as analysis of scientific literature, indicated that dynamical chaotic models could describe flow and transport in heterogeneous fractured rocks.

The primary objectives of this project are:

(1) To determine if and when dynamical chaos theory can be used to investigate infiltration of fluid and contaminant transport in heterogeneous soils and fractured rocks, and
(2) To introduce a new approach to the multi-scale characterization of flow and transport in the fractured basalt of the vadose zone and to develop physically based conceptual models on a hierarchy of scales.

Research Progress and Implications

The objectives of this project are being achieved through the following accomplishments:

- Series of ponded infiltration tests, including (1) Small-scale infiltration tests (ponded area 0.5 m^2) conducted at the Hell's Half Acre site near Shelly, Idaho and (2) intermediate-scale infiltration tests (ponded area 56 m^2) conducted at the Box Canyon site near Arco, Idaho;
- Laboratory investigations and modeling of flow in a fractured basalt core;
- Series of small-scale water dripping experiments in fracture models conducted to evaluate chaotic behavior of flow in single fractures;
- Development of a conceptual model and mathematical and numerical algorithms for flow and transport, which incorporate both (a) the spatial variability of heterogeneous porous and fractured media, and (b) the description of the temporal dynamics of flow and transport, which may be chaotic; and
- Development of appropriate experimental field and laboratory techniques needed to determine diagnostic parameters for chaotic behavior of flow.

The main hypothesis tested in this project is:

"Subsurface spatial and temporal heterogeneity, non-linear feedback between unsaturated hydraulic processes and parameters, such as unsaturated hydraulic conductivity, moisture content, entrapped air, non-uniform matrix surface geochemistry and numerous other factors affect vadose zone flow and transport such that chaos theory can be used to describe the vadose zone process".

This past year's efforts culminated a three-year project that included ponded infiltration tests conducted in Idaho at two fractured rock field sites: the Hell's Half Acre (the scale of 1 by 0.5 m) and the Box Canyon (the scale of 7 by 8 m) sites. Monitoring of water dripping, geophysical imaging, in-situ measurements of the moisture content, water flow, water pressure in the rock matrix and fractures, tracer distribution, and other critical parameters were used to characterize the temporal and spatial

evolution of chaotic behavior at the meter scale in unsaturated fractured rock for the first time. Several new technologies have been developed for this project including piezoelectric probes, a leak detection system, a laser surveying system, and a 3D Electrical Resistivity Tomography system. During the last year, we also refined the modeling approaches and wrote six technical reports and scientific papers, submitted for publication.

Laboratory experiments were conducted to evaluate the presence of chaotic behavior in water seepage through fracture models. The pervasiveness of highly localized and extremely non-uniform flow paths in the plane of the fracture was shown. Using the time-trend of a pressure signal for unsaturated flow in fracture models, the magnitudes of deterministic-chaotic and stochastic components in the data were analyzed. For this purpose, several parameters were determined such as the correlation time, Hurst exponent, Lyapunov exponent, capacity dimension, correlation dimension, and information entropy. The time-series data were used to construct three-dimensional attractors in a phase-space.

Numerical modeling of the Box Canyon ponded infiltration tests using the TOUGH2 code with an explicit, yet simplified, representation of the key geologic and hydrogeological features (a hierarchical pattern of column-bounding and column-normal fractures in fractured basalt) confirmed (a) the presence of complex, irregular flow paths for liquid-phase tracer, as well as air trapping and escaping in the vadose zone, and (b) the temporal aspects of chaotic flow, identified in laboratory and field experiments, cannot be captured using conventional modeling approaches.

Theoretical studies have shown that as a fluid film flows on an inclined fracture surface, is inherently unstable and may exhibit chaotic behavior, even for low Reynold's numbers. Film waviness may enhance transfer of contaminants from rock to fluid by as much as five times carrying contaminated fluid down a fracture much faster than expected by classical flat film theory.

Relevance, application, impact and technology transfer issues. The results of this project can be used by DOE to demonstrate the complex behavior of vadose zone transport and for development of characterization and monitoring methods, predictions, and the design of remediation approaches at contaminated sites, such as, Hanford, INEEL, LLNL, Oak Ridge, and LBNL.

The information and techniques developed from this project address numerous gaps identified in the book prepared by the Subsurface Contaminants Focus Area, and can directly be applied to formulating cleanup strategies for contaminants in the vadose zone. Three sites that can benefit from the findings of this work include the Underground Test Area at the Nevada Test Site, the vadose zone below the Hanford tanks, and the Radioactive Waste Management Complex of the INEEL. This project enables a better understanding of plume delineation and spreading rate so that applied cleanup technologies can be optimized.

Value/Benefits. The scientific and practical values of this approach are that we hope to determine the range within which the parameters of flow and transport will occur based upon the collection of a limited data set. Albeit, we cannot predict the behavior at any point or time. This is similar to saying we can determine the climate for a certain geographic province, but are unable to predict the temperature on any given day. The current reductionist approach to numerical modeling of vadose zone transport assumes that by knowing with enough certainty all of the subsurface factors affecting flow, we can predict with accuracy the temperature on any given day (or the temperature range). The uncertainty of this reductionsist approach has lead to several surprising "detections" of contaminants afield of DOE Facilities (Board on Radioactive Waste Management, 1999).

The scientific issues of the research rests in (a) the unique non-linear dynamics analysis of data sets such as fracture and matrix flow rates, pressure, and tracer concentrations, and (b) the development of a new dynamical chaotic model for flow and transport in fractured media. The results of this project are expected to change the conventional approach of using traditional stochastic and/or deterministic methods to predict flow and transport in environmental systems. Because the non-linearity of environmental systems limits their predictability into the future, we aim to determine how far into the future it is realistic to predict the state of the environmental system, and what the bounds on the time of contaminant transport are, and how long DOE will need to provide stewardship of theses sites. The significance of the research for the DOE will be in the form of new technologies developed for vadose zone monitoring and in improved vadose zone site characterization and predictability.

Improved information on contaminant transport and concentrations enables the development of better, more cost effective and protective cleanup strategies. Optimization of cleanup strategies based upon reliable predictions of contaminant fate and transport will save costs, shorten schedules and increase DOE credibility with stakeholders. Through improved understanding of contaminant spread drinking water sources, health and safety risks to surrounding populations will be minimized.

Collaborative work. Long-term collaboration between the LBNL and INEEL allowed us to better understand the practical problems facing DOE sites and use the potentials of both DOE Laboratories. Investigations were conducted in collaboration with University of Nevada, Reno, Geological Survey of Canada, Alberta Research Council of Canada, Lawrence Livermore National Laboratory, University of California at San Diego, and University of Alabama, Tuscaloosa, Alabama. Three graduate studies were also funded under this EMSP project.

Partitioning Tracers for In-Situ Detection and Quantification of Dense Nonaqueous Phase Liquids in Groundwater Systems

Project ID: 54908

Dr. Mark L. Brusseau, University of Arizona

Mart Oostrom, Pacific Northwest National Laboratory
Mark White, Pacific Northwest National Laboratory

Research Objective

The overall goal of the project is to explore the use of an innovative in-situ method (partitioning tracer tests) for detection and quantification of dense nonaqueous phase liquids (DNAPLs) in subsurface systems. DNAPLs occur in the subsurface at numerous contaminated sites and can act as long-term sources of groundwater contamination. Both effective risk assessment and remediation of DNAPL-contaminated sites is limited by current site characterization techniques. A major limitation of the current methods is that they provide data at discrete points, such that the probability of sampling a zone of localized DNAPL is quite small. The results of this research will lead to an improved method for characterizing DNAPL-contaminated sites and will enhance our understanding of the distribution of immiscible liquids in the subsurface. The use of this method will help reduce the uncertainty associated with risk assessments and remediation planning.

Research Progress and Implications

This report summarizes work completed mid-way through year three of this project. During the past year, we have: (1) conducted a set of experiments in an intermediate-scale flow cell to examine the impact of heterogeneity and sampling method on the performance of the partitioning tracer method; (2) conducted a set of preliminary experiments in an intermediate-scale weighing lysimeter to evaluate the efficacy of a gas-phase partitioning tracer method for measuring soil-water content; (3) conducted several sets of experiments in the laboratory to continue to search for viable partitioning tracers; and (4) critically reviewed and summarized published applications of the partitioning tracer method. The results of these efforts are summarized below, with a focus on the first two items.

The purpose of this set of experiments was to examine the effect of porous-media heterogeneity, nonuniform distribution of DNAPL, and sampling method on the performance of the partitioning tracer method for measuring DNAPL saturation in water-saturated subsurface systems. Experiments were conducted in an intermediate-scale flow cell (2m x 1m x 0.06m) containing two discrete zones of trichloroethene (TCE) at residual saturation. One zone (Zone 2) consisted of ~10% saturation formed in the same sand as used for the flow-cell matrix. The other zone (Zone 1) consisted of ~10% saturation in a finer sand emplaced within the coarser matrix. Aqueous samples were collected using depth-specific sampling, vertically integrated sampling, and at the extraction well. A dual-energy gamma radiation system was used to measure TCE saturation before and after the tracer experiment, allowing the measurements obtained from the tracer experiment to be compared to a previously tested method. The saturations estimated using the data collected at point-sampling ports located downgradient of Zones 1 and 2 were approximately 7% and 50% of the true values, respectively. The saturations estimated using the data obtained from the vertically-integrated ports were 2% and 0% of the true values, respectively. Finally, the saturation estimated using the extraction-well data was 30% of the cell-wide averaged value. These results indicate that the presence of porous-media heterogeneity and a variable distribution of DNAPL saturation can lead to reduced accuracy of the

partitioning tracer test. The reduced performance can be improved, in part, by using depth-specific sampling.

The purpose of this set of experiments was to evaluate a gas-phase partitioning tracer method for the in-situ measurement of soil-water content in water-unsaturated systems. The method is based on the use of a tracer test with non-partitioning and partitioning tracers introduced into the system in the gas phase. Experiments were conducted in the laboratory and in a large weighing lysimeter (2.5m x 4m) to test the performance of the gas-phase partitioning tracer method. Soil-water contents estimated from the tracer tests were reasonably close to values obtained using gravimetric and time domain reflectometry measurements, indicating the gas-phase tracer method has the potential to provide accurate measurements of soil-water content at the field scale.

Planned Activities

We are currently conducting a second set of experiments with the intermediate-scale flow cell mentioned above. One objective of this new work is to examine the impact of a DNAPL pool on the performance of the partitioning tracer method. Another objective is to examine the impact of temporal variability of DNAPL saturation (e.g., due to dissolution) on the performance of the partitioning tracer method.

Information Access

Nelson, N.T., M. Oostrom, T.W. Wietsma, M.L. Brusseau; The Partitioning Tracer Method for the In-Situ Measurement of DNAPL Saturation: Influence of Heterogeneity and Sampling Method. Environ. Sci. Technol., 1999 (in review).

Nelson, N.T., M.L. Brusseau, T.D. Carlson, M.H. Young, G.R. Johnson, M.S. Costanza, and P.J. Wierenga; A Gas-phase Partitioning Tracer Method for the In-situ Measurement of Soil-water Content. Water Resour. Res., 1999 (in review).

Brusseau, M.L., N.T. Nelson, M.S. Costanza; Partitioning Tracer Tests for Characterizing Immiscible-fluid Saturations and Interfacial Areas in Subsurface Systems, 1999 (in review).

New Permeameters for In Situ Characterization of Unsaturated Heterogeneous Permeability: Development, Design, Testing, and Application

Project ID: 55109

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Robert J. Glass, Sandia National Laboratories - Albuquerque

Research Objectives

Thick unsaturated zones underlie many Department of Energy (DOE) landfills, industrial areas, and waste storage sites in the western United States and are the primary pathway for contaminants to migrate into underlying aquifers. The spatial variability of unsaturated hydraulic properties in these heterogeneous geologic materials directly influences the movement of water and non-aqueous phase liquids (NAPL's). Poor characterization of heterogeneity may lead to ineffective remedial designs and increased risk, requiring subsequent additional remedial actions at increased cost and time. Remedial design can be improved using probabilistic risk-based decision analysis, which requires a large number of hydraulic property observations. Laboratory methods for estimating the unsaturated permeability are expensive, time-consuming, and may not yield results representative of heterogeneous field conditions. Simple and rapid field methods for estimating *in situ* unsaturated permeability are appealing and potentially cost-effective.

The primary objective of our EMSP research is to design, develop, and test new permeameters for use in spatial variability studies. We have established a series of permeameter design criteria, including: 1) measurements should be relatively rapid, 2) the total cost per data point should be low, 3) results would accurately reflect the variation of unsaturated hydraulic properties between sampled locations, 4) the volume sampled (measurement support) would be small, and 5) useful range would be relevant to the range of soil moisture conditions encountered at DOE sites

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Research Progress and Implications

This report summarizes work after year three of a three year project. We have requested a one year no-cost extension. In past years we have reported our activities related to development and testing of techniques for inverting permeameter data, development of numerical tools for data inversion, error evaluation for permeameter design, and permeameter component design. This year, however, the results of our error evaluation for permeameter design have caused us to redirect our research, and we focus on the results of these studies and their implications for our research. We now believe that it is not possible, given our current mathematical models for unsaturated flow and the range of possible instruments, to reliably estimate, from *in situ* measurements, the spatial statistics of parameters that describe the slope of the pressure-saturation and relative-permeability curves.

We evaluated the effect of error on the uncertainty of estimated spatial statistics to improve permeameter designs. Hydraulic properties (e.g., hydraulic conductivity) are estimated using an observed system response to invert a mathematical model of an experiment. Errors in estimates of hydraulic properties (property-estimation errors) arise from both measurement and inversion-model errors. Because property-estimation errors are correlated with the sampled hydraulic property and are not mean-zero, estimated spatial statistics of hydraulic properties are biased and uncertain.

Measurement errors result from erroneous, direct observation of system or device states (e.g., pressure, flow rate, and the location of observation points) and are non-linearly propagated through

the inverse solution for the hydraulic property. Because measurement errors are a function of the hydraulic response of the sampled system and the "true" value of the hydraulic property, estimation errors are likely to be correlated with the true hydraulic-property.

Inversion model error results when the fundamental assumptions of the inversion model are invalid. This type of error can result from an incorrect mathematical model, an inappropriate parametric model, sub-sample-scale heterogeneity, scaling-effects, boundary condition errors, and other unresolved or ill-described physics. Most inversion-model errors introduce systematic errors in the estimated hydraulic property and can be correlated with the true values of the sampled field.

We evaluated bias and uncertainty in the spatial statistics of unsaturated hydraulic properties estimated with a tension infiltrometer, a field device commonly used for examining the spatial variability of unsaturated hydraulic properties. We considered only small measurement errors affecting the observed flux-rate from the device, small measurement errors in the applied device pressure, and an error in the contact between the device and the sampled medium. We neglected other, more serious, forms of inversion-model error, including: hysterisis, air entrapment, sub-sample-scale heterogeneity, and fluid-viscosity changes. We used a Monte Carlo approach to propagate our simple errors through steady-state, analytical inversions for hydraulic properties, and we evaluated the bias and uncertainty in spatial statistics of our estimated hydraulic properties. In the hydraulic property range of materials likely to be encountered at DOE sites, estimated hydraulic properties were strongly biased, and their spatial statistics reflected this bias and were highly uncertain. Bias and uncertainty increased when boundary-condition error was also considered. Because the tension infiltrometer performed very poorly under nearly ideal conditions, we concluded that the tension infiltrometer cannot reliably estimate hydraulic properties for spatial variability studies. Other approaches for estimating unsaturated permeability (e.g., transient methods) require more complicated inversion models, which are likely to be more sensitive to measurement and inversion-model errors.

Because the tension permeameter performed so poorly for estimating the spatial statistics of *in situ* unsaturated hydraulic properties, we evaluated property-estimation errors inherent to laboratory methods for estimating unsaturated hydraulic properties and their impact on estimates of spatial statistics. In principle, laboratory methods provide the most accurate estimates of unsaturated hydraulic properties, because inversion models are simple and subject to fewer sources of error. We directly evaluated, using Monte Carlo methods, the influence of property-estimation errors on spatial statistics for parameters that describe the moisture-retention curve and unsaturated hydraulic conductivity. Our results indicate that very small amounts of measurement error introduce little bias or additional uncertainty in estimated spatial statistics for hydraulic properties that scale the unsaturated hydraulic conductivity and moisture-retention curves (saturated hydraulic conductivity, porosity, and air entry value). Spatial statistics for parameters related to the slope of the relative permeability and pressure-saturation curves, however, are moderately to very strongly biased by property-estimation errors and are substantially more uncertain. Our results represent a "best" case, as the measurement errors used were very small and a variety of errors (air entrapment, alteration of sample properties during removal and experiments, etc.) were neglected. We conclude that laboratory methods may not be capable of generating reliable estimates of spatial statistics for model parameters that describe the slope of the relative permeability and moisture-retention curves, especially in the presence of more realistic errors.

We now believe that the spatial statistics of parameters that describe the slopes of the pressure-saturation and relative permeability curves cannot be reliably estimated using either field or laboratory methods, even under nearly ideal conditions. As a result, we have shifted the focus of our research and placed emphasis on estimating those parameters that scale the pressure-saturation and relative permeability curves (saturated hydraulic conductivity and air-entry pressure) and surrogate methods for estimating the slope parameters. Preliminary error analysis of direct methods for estimating the saturated hydraulic conductivity (air permeameter) and air-entry pressure (air-entry permeameter) indicate that spatial statistics for these parameters can be reliably estimated in the field. Surrogate methods for estimating the slope of the pressure-saturation and relative permeability curves from these data appear to perform worse than laboratory methods but much better than *in situ* measurement techniques (e.g., the tension infiltrometer).

Our preliminary permeameter design now consists of a modification of the air mini-permeameter device with a water-flow apparatus for saturating the sampled area. The air permeability is measured,

the sample area is saturated, and the air-entry pressure is measured. Preliminary laboratory testing of an air-entry permeameter has been successful.

Planned Activities

We will continue to refine and finalize our permeameter design and construct a field prototype. Measurement errors for our device will be quantified based upon laboratory testing. Using the statistics of our measurement errors, we will evaluate bias and uncertainty affecting spatial statistics of unsaturated hydraulic properties estimated with our device. This will serve to identify the material types where our device will yield accurate estimate spatial statistics of unsaturated hydraulic properties. Our final activity will be a field demonstration of the final permeameter design. A field test site has already been selected, and permeameter testing will be performed at a U.S. DOE EMSP project site (A Hybrid Hydrogeologic - Geophysical Inverse Technique for the Characterization, Monitoring, and Risk Assessment of Leachates in the Vadose Zone) in Socorro, New Mexico.

In Situ, Field Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well, Push-Pull Test

Project ID: 55196

Dr. Jonathan D. Istok, Oregon State University

Jennifer A. Field, Oregon State University

Research Objective

The overall goal of this project is to further develop the single-well, "push-pull" test method as a site characterization and feasibility assessment tool for studying the fundamental fate and transport behavior of injected surfactants and their ability to solubilize and mobilize DNAPLs in the subsurface. To address the three objectives, the research plan combines controlled intermediate-scale laboratory experiments in unique physical aquifer models with a parallel series of pilot-scale field experiments in existing monitoring wells at selected trichloroethene (TCE) contaminated field sites.

Research Progress and Implications

Sorption to aquifer sediments can limit the effectiveness of surfactants injected to solubilize residual nonaqueous phase liquid contaminants in the subsurface. A study was conducted to evaluate the ability of the single-well, push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment *in situ*. The results demonstrated the ability of the push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment under laboratory and *in situ* field conditions. Increased retardation and chromatographic separation of LAS homologs relative to Br^- observed during laboratory push-pull tests could not be accurately described by numerical transport simulations based on fitted sorption isotherms obtained from batch sorption experiments. Better agreement was obtained between simulated and observed breakthrough curves for DOWFAX; however, simulations predicted slight retardation for DOWFAX that was not observed in either laboratory or field push-pull tests. We attribute these differences to the inability of batch sorption isotherms to accurately represent *in situ* conditions. In particular, simulations based on batch sorption isotherms produced for a commercial surfactant mixture can not accurately describe surfactant transport when the composition of the surfactant mixture changes (e.g. due to chromatographic separation) during transport. Moreover, equilibrium sorption isotherms produced in batch experiments cannot describe the kinetically-limited sorption of a surfactant that potentially occurs during transport in the highly nonuniform pore water velocity field around an injection well.

However, generally close agreement was observed for extraction phase breakthrough curves for LAS and DOWFAX in laboratory and field push-pull tests. Retardation and chromatographic separation of LAS homologs observed in breakthrough curves and mass recovery plots from laboratory push-pull tests were clearly visible in breakthrough curves and mass recovery plots for field push-pull tests conducted *in situ*. Based on the results of this study, the single-well, push-pull test appears to be a useful method for obtaining site-specific information on the sorption behavior of injected surfactants (or other solutes). The method can be applied in existing monitoring wells without the need for sediment cores and appears to provide results that are more representative of *in situ* conditions than laboratory batch sorption experiments. It should also be noted that the laboratory and field push-pull tests confirmed that information on sorption characteristics of an injected solute can be obtained from only the extraction phase breakthrough curves, without the need for observations at

additional monitoring wells. The method should be particularly useful for selecting and evaluating surfactants as part of a feasibility assessment. In addition, the method can be used to perform small-scale pilot tests because the test conditions closely approximate those occurring in the vicinity of injection wells that will be used in full-scale surfactant-enhanced NAPL recovery systems. The method also provides a simple and rapid method for characterizing the *in situ* transport behavior of any solute without the need for sediment cores.

A second study was conducted to evaluate the ability of the push-pull test to characterize enhanced solubilization of TCE by a hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactant. The results of intermediate-scale laboratory experiments indicate that the single-well, push-pull test method can provide quantitative information on the effectiveness of injected surfactants in enhancing liquid TCE solubilization in natural aquifer sediments. Push-pull test extraction phase breakthrough curves can be used (1) to examine surfactant transport behavior relative to that of a coinjected tracer; (2) to determine the recovery efficiency of an injected surfactant, and (3) to quantify the increase in aqueous TCE solubility due to injected surfactant.

Batch solubilization experiments indicated a linear relationship between TCE solubility and DOWFAX concentration characterized by weight- and molar-solubilization ratios of 0.26 and 1.25, respectively. Laboratory push-pull tests were performed in wedge-shaped physical aquifer models to simulate the alternating radially divergent/convergent flow field in the vicinity of an injection/extraction well. Experiments were conducted in a TCE-free sediment pack and in a sediment pack initially containing liquid TCE with an initial saturation of ~ 5 % of the total pore volume. In an experiment conducted in the absence of DOWFAX, maximum TCE concentrations during the extraction phase were ~ 0.6 g/L. In contrast, in an experiment conducted with 13.5 g/L active DOWFAX, TCE concentrations during the extraction phase increased to ~ 3.2 g/L and TCE mass recovery increased by a factor of ~ 3. Two additional experiments conducted with DOWFAX in the same sediment pack yielded smaller maximum TCE concentrations and mass recoveries. The increased density of injected DOWFAX solutions due to TCE solubilization resulted in significant sinking of injected solutions and an accumulation of DOWFAX and TCE at greater depths in the sediment pack; however, no mobilization or sinking of liquid TCE was observed.

A third study was conducted to evaluate the influence of cation exchange on the solubilization of residual TCE by the surfactant sodium dihexyl sulfosuccinate (Aerosol MA 80-I). Laboratory transport experiments were conducted using natural aquifer sediment collected or obtained from a TCE-contaminated field site and a test solution consisting of 36,800 mg/L sulfosuccinate surfactant, 100,000 mg/L isopropanol, and 3,200 mg/L KBr. Laboratory experiments were designed to simulate conditions occurring during field push-pull tests. In batch experiments conducted in the presence of excess TCE, the test solution gave a Winsor Type I system with an enhanced aqueous TCE solubility of 26,700 mg/L and a solution density of 1.0000 g/cm^3. The sulfosuccinate surfactant was transported conservatively in sediment packs containing no TCE; however, increased concentrations of Ca^{2+} and Mg^{2+} were observed, which resulted from cation exchange. Sulfosuccinate surfactant transport was strongly retarded in sediment packs containing 5 vol % residual TCE because cation exchange in the presence of liquid TCE resulted in the formation of a Winsor Type II system and resulted in the partitioning of the sulfosuccinate surfactant into the stationary TCE phase. Conservative sulfosuccinate transport was observed in a separate sediment pack containing 5 vol % residual TCE when a 130 mM NaCl pre-flush was used to reduce quantities of Ca^{2+} and Mg^{2+} in the sediment pack prior to sulfosuccinate injection. The results of this study emphasize the potentially detrimental effects of cation exchange on surfactant performance and enhanced TCE solubilization and demonstrate the utility of the push-pull test for predicting the effects of cation exchange on surfactant phase behavior in the presence of residual TCE.

In the final study of this project, we examined the ability of a modified push-pull test method for predicting cation exchange and the effects it will have on surfactant performance *without* the addition of surfactants to the subsurface. Our approach consists of injecting a simple salt solution to displace cations from the sediment, which simulates what would occur if a surfactant and its attendant salt were injected. A series of laboratory push-pull tests were performed in physical aquifer models designed to simulate conditions occurring near an injection/extraction well during a field test. Three physical models were packed with clean silica sand and two natural sediments. Injected test solutions contained

30 mM KBr to simulate the amount of salt typically added to the anionic surfactant Aerosol MA 80-I to promote Winsor Type I phase behavior and optimal TCE solubility. Porewater samples were collected from the sediment pack and analyzed for Na^+, K^+, Ca^{2+}, Mg^{2+}, and Br^-. In addition, the collected samples were combined with surfactant (Aerosol MA 80-I) and liquid TCE and analyzed for aqueous phase surfactant and TCE concentrations. Samples collected during experiments conducted in clean silica sand, which had minimal cation exchange capacity, had low divalent/monovalent cation ratios and gave aqueous phase TCE concentrations essentially identical to those predicted from batch solubilization isotherms. In contrast, samples collected during experiments conducted in both natural sediments (which had similar cation exchange capacities of approximately 20 meq/100 gm) had divalent/monovalent cation ratios large enough to cause aqueous phase TCE concentrations to exceed those predicted from the batch isotherm. In previous work with these sediments and surfactant, the occurrence of TCE solubilization potentials larger than those predicted by the batch isotherm corresponded with the formation of Winsor Type II behavior and the partitioning of injected surfactant into the residual TCE phase. Thus, a push-pull test conducted with a low concentration of salt can be used as a low risk, low cost tool for predicting the deleterious effects of cation exchange on surfactant effectiveness.

Planned Activities

This project will conclude in September, 1999. The remainder of project resources will be devoted to completing manuscripts in progress and in dissiminating research results to potential technology users.

Publications

Field, J.A., T.E. Sawyer, M.H. Schroth, and J.D. Istok. 199X. Effect of Cation Exchange on Surfactant Enhanced Solubilization of Trichloroethene. Submitted to Journal of Contaminant Hydrology

Schroth, M.H., J.D. Istok, and R. Haggerty. 199X. "In-Situ Evaluation of Solute Retardation Using Single-Well Push-Pull Tests". Submitted to Journal of Hydrology.

Field, J.A., J.D. Istok, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey. 199X. Laboratory Investigation of Surfactant-Enhanced TCE Solubilization Using Single-Well, "Push-Pull" Tests. Ground Water (In Press).

Istok, J.D., J.A. Field, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey. 199X. Laboratory and Field Investigation of Surfactant Sorption Using Single-Well, "Push-Pull" Tests. Ground Water (In Press).

Field, J.A. and J.D. Istok. 199X. Comment on Estimation of Nonaqueous Phase Liquid-Water Interfacial Areas in Porous Media Following Mobilization by Chemical Flooding. Environmental Science and Technology, Vol. 32, No. 2, pp. 3836-3837.

Colloid Transport and Retention in Fractured Media

Project ID: 55036

John F. McCarthy, Oak Ridge National Laboratory

Larry D. McKay, University of Tennessee
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Motomu Ibaraki, Ohio State University

Research Objectives

The goal of the project entitled "Colloid Transport and Retention in Fractured Media" was to identify the chemical and physical factors that control the transport of colloids in water-saturated fractured formations, and develop a generalized capability to predict colloid attachment and detachment based on hydraulic factors, physical structure, and chemical properties. The research targeted multiple scales, including (a) mechanistic description and experiments colloid dynamics in fractures; (b) colloid transport experiments in undisturbed geological monoliths; (c) field-scale colloid transport experiments; and (d) modeling of colloid transport in complex fracture networks.

Research Progress and Implications

Fundamental Description Of Particle Transport In Fractures – Using first principles, models were developed for particle deposition rate on the surface of fractures and results experimentally tested. The model is similar to those presented by Friedlander, Cookson, and Yao et al. for describing aerosol and aqueous filtration by stationary collectors, but is unique in accounting for the geometry of the collector surface; in this case, infinite planes of two separated by a finite aperture width. Using a particle tracking method, an algorithm has been developed to describe the colloid dynamics in fractures, including consideration of particle diffusion, sedimentation under gravity field, and electrostatic interactions of colloids with fracture walls under infinite plane geometry. A steady state solution is attained. The particle diffusion and collection by walls are most significant, compared to gravitational sedimentation. We have also derived an analytical solution for large Peclet numbers under steady state (expressed in terms of parabolic cylinder functions), and confirmed agreement between this solution and the steady state solution given by the particle-tracking model. An experimental system of 1-D parallel-plate artificial fracture with SiO_2-coated fracture walls was used to test and validate the model predictions (Fig. 1). The advanced mechanistically rigorous descriptions of colloid migration under infinite plane geometry will be incorporated in models of colloid transport in water films within partially saturated media.

Colloid Transport In Intact Geological Columns – Colloid tracer experiments using undisturbed monoliths of fractured saprolite under water-saturated conditions investigated the influence of particle diameter and the ionic strength and cation valence of the groundwater solution. There was an optimum size of 0.5 to 1.0 μm for transport of the latex microsphere tracers. Loss of the smaller-than-optimum particles was attributed to the more rapid diffusion of the smaller particles, leading to more collisions with, and retention by, the fracture walls. This was confirmed by dismantling of the core and mapping of distribution of the microspheres using petrographic thin sections and epifluorescent microscopy to visualize the fluorescent colloids. In experiments using aqueous solutions containing different ionic strengths of monovalent (Na^+) and divalent (Ca^{2+}) cations, colloid retention increased as ionic strength increased, with far greater retention with the divalent cations (Fig. 2).

Field-Scale Colloid Tracer Migration — Two series of field tracer experiments were completed. In the first experiment was conducted at a radionuclide-contaminated DOE site at which groundwater contained near-saturated levels of $CaCO_3$. Colloid transport was very limited (Fig. 3), consistent

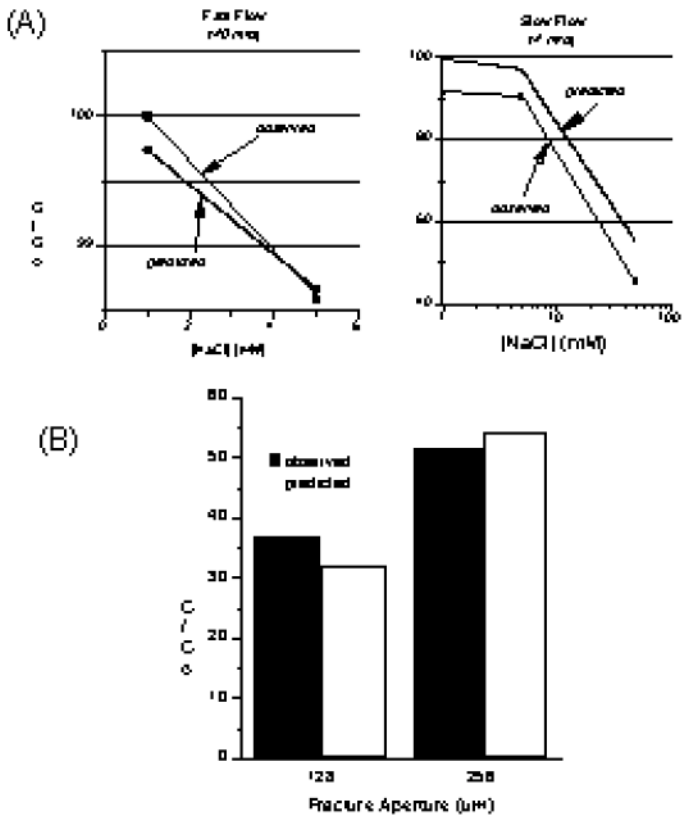


Figure 1. Comparison of analytical model predictions with experimental observations of colloid transport in artificial fracture apparatus. (A) Effect of flow rate and ionic strength on colloid transport through model fractures; (B) Effect of aperture width on colloid transport.

with the effects of high Ca levels observed in the column studies. However, colloids retained by the formation could be mobilized by experimental manipulation of ionic strength that increased the concentration of colloids by two orders of magnitude within a few days. Hypotheses concerning the effects of water chemistry and fracture network characteristics were tested at the second experimental site. The ionic strength of the groundwater at the second site was less than half that at the first site; furthermore, colloids were injected into wells screened in two contrasting lithologies: a highly weathered saprolite similar to the intact column (characterized by a dense network of small fractures), and an underlying rubbly, weathered bedrock (characterized by larger, more widely-spaced fractures). Data (Fig. 3) revealed 1) there is considerably greater mobility of colloids at the second site compared to the first site, consistent with the lower ionic strength, and 2) that there are very significant differences in the rate and extent of colloid transport in the two lithologies, with much greater retention of small colloids in the densely-fractured upper zone. These results are consistent with the ionic strength studies at the column scale (above), and with predictions from the fracture network model (below).

Fracture Network Models of Colloid Transport – Numerical simulations of colloid transport in discretely fractured porous media investigated the importance of diffusion into fine porosity as well as the retention and remobilization of colloids. The processes accounted for by the finite element code, COLDIFF, include advective-dispersive transport of colloids, filtration and mobilization of colloidal particles in both fractures and porous media, and diffusive interactions of colloids between the fractures and porous media. Results demonstrated the importance of the porosity of the matrix and colloid retention. Simulations successfully reproduced observed transport data in saprolite monoliths (Fig. 4), and highlighted the tailing caused by remobilization of colloids after the source was removed. Field-scale simulations indicated that diffusive transfer of colloids to fine porosity and colloid retention and remobilization on fracture walls were dominant processes affecting the long-

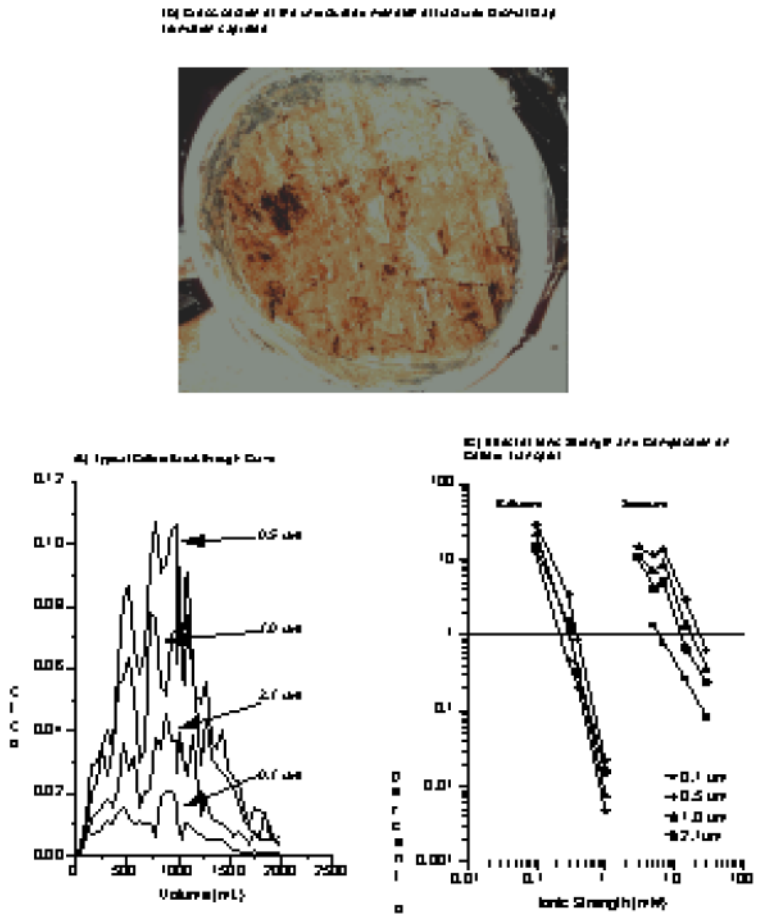


Figure 2. Colloid transport in undisturbed monoliths of saturated fractured saprolite from the Dismal Gap formation (Oak Ridge National Laboratory)

term colloid concentration and migration distance. In environments where porosity is relatively high and colloids are able to diffuse from the fractures, the properties of the porous matrix were more important than those of the fracture network. Because the properties of the fracture network are more difficult to know with certainty relative to those of the porous matrix, predictive uncertainties associated with colloid transport in discretely fractured porous media may be reduced.

Summary and Implications – Both aqueous chemistry and physical structure of geologic formations influence transport. Results of studies at all spatial scales reached consensus on the importance of several key controlling variables: 1) not unexpectedly, colloid retention is dominated by chemical conditions favoring colloid-wall interactions; 2) even in the presence of conditions favorable to colloid collection, deposited colloids are remobilized over long times and this process contributes substantially to the overall extent of transport; 3) diffusive exchange between water-conducting fractures and finer fractures and pores acts to "buffer" the effects of the major fracture network structure, and reduces predictive uncertainties. Predictive tools were developed that account for fundamental mechanisms of colloid dynamics in fracture geometry, and linked to larger-scale processes in networks of fractures. Although a great deal more remains to be learned about colloid transport in water-saturated media, the results of our study highlight the key role of physical and hydrologic factors, and processes of colloid remobilization that are potentially of even greater importance to colloid transport in the vadose zone than in saturated conditions. We therefore propose to focus this

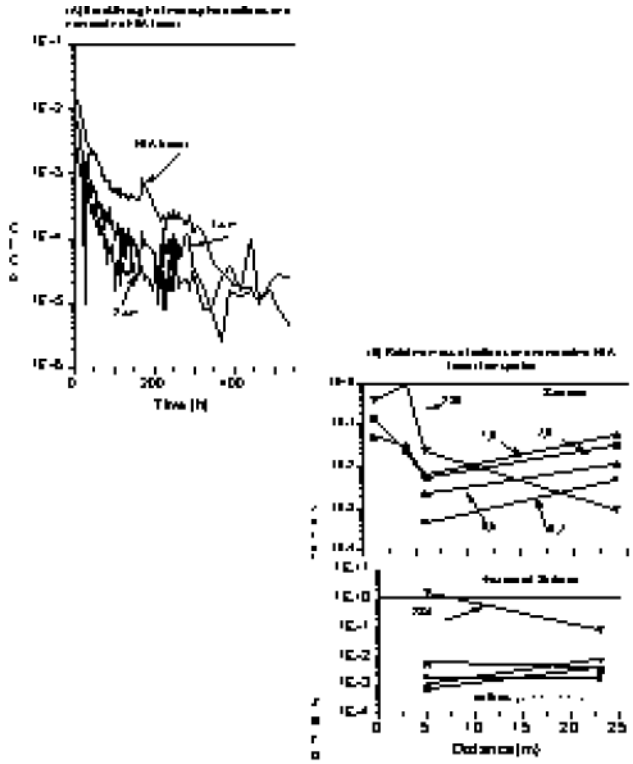
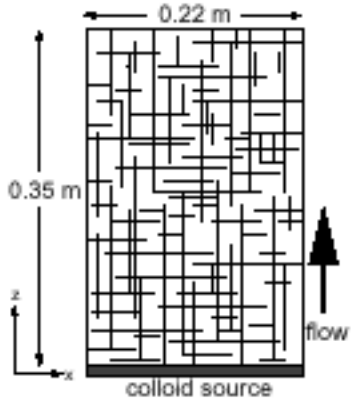


Fig. 3. Field-scale transport of different sizes of carboxylate-modified latex microspheres through water-saturated fractured formations. (A) Breakthrough of microspheres over a 3-m flow path of fractured aquifer. Note that colloids were injected for a 4-h period, yet deposited colloids continued to be released from the formation over extended times. (B) The relative mass of colloids (each marker) of colloids injected into two lithologies at the same location.



proposal on understanding vadose zone transport processes so that they can eventually be linked to the understanding and tools developed in our previous project on transport in saturated groundwater systems.

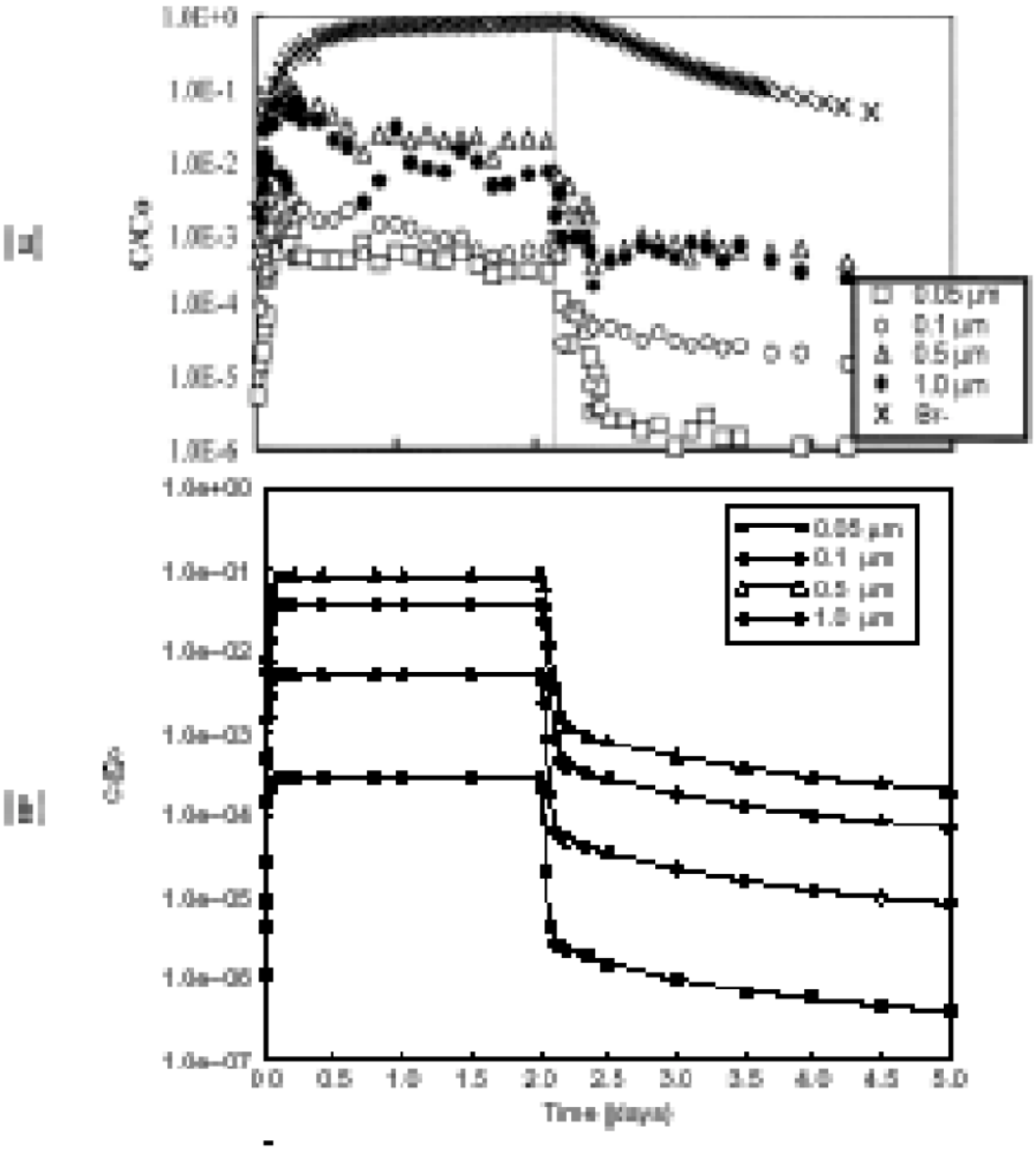


Fig. 4. Comparison of observed data and network model simulation of colloid transport through an undisturbed monolith of Dismal Gap saprolite. The top panel is the representation of the experimental core for the network model. The graphs show the relative concentration rations (C/Co) for the laboratory core-scale experiment and the results of the numerical simulation performed using COLDIFF.

Behavior of Dense, Immiscible Solvents in Fractured Clay-rich Soils

Project ID: 55083

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John Sanseverino, University of Tennessee
Phillip M. Jardine, Oak Ridge National Laboratory
Scott C. Brooks, Oak Ridge National Laboratory
John A. Cherry, University of Waterloo
Beth L. Parker, University of Waterloo

Research Objective

This research program addresses the nature and distribution of chlorinated solvent DNAPL sources in fractured clays and weathered shales, and the potential for natural attenuation of plumes derived from these sources.

Specific objectives include:

1. Investigate the factors controlling migration of chlorinated solvent DNAPLs in fine-grained, highly structured soils and weathered shale bedrock.
2. Investigate the influence of "matrix diffusion" on the dissolution and apparent disappearance of residual DNAPL.
3. Investigate potential for biodegradation of chlorinated solvents in fractured and weathered shales at an existing contaminated field site and through the use of laboratory studies in microcosms and undisturbed columns of fractured shale saprolite.
4. Comparison of DNAPL behavior in different types of fractured clay-rich materials.

Research Progress and Implications

This report summarizes progress made during the first 3.5 years of a 4-year project (now on a no-cost extension). The project investigates the behavior of chlorinated solvent DNAPLs (mainly TCE) in two fractured clay-rich materials: highly weathered shale saprolite at Oak Ridge National Laboratory in eastern Tennessee; and weathered glacial till in southwestern Ontario, Canada.

Weathered and Fractured Shale Saprolite Column Experiments

Air/water and DNAPL/water entry and pressure-saturation curves have been experimentally measured for an undisturbed column sample of fractured weathered shale from Oak Ridge National Laboratory (ORNL). Preliminary evaluation showed that typical fractures in saprolite are sufficiently large to allow entry of DNAPL even for very small spills (capillary pressure head values of 5-8 cm). The experiments also show a relatively low matrix pore entry pressure (160-210 cm of head), indicating that at many sites DNAPL is likely to enter both the fractures and the matrix, where it would be virtually impossible to remove with DNAPL recovery wells. A second series of experiments was recently completed to measure DNAPL distribution in the fractures and matrix for simulated spills. This data is currently being studied and a paper is in preparation.

Matrix Porosity and Pore Size Investigations in Weathered Shale Saprolite

Investigations of porosity and pore size distribution have been carried out and they indicate that there is a wide range of fracture and matrix pore types and sizes in the saprolite. Many of the most prominent fractures are infilled with pedogenic clays, so it is often the less prominent features that are conductive. The thin-sections also showed that there is much greater variability in the matrix lithology and pore size distribution than previously expected. In some regions of a sample, matrix pores might be largely filled with pedogenic clays or Fe/Mn oxides, while only a few cm's away the pores were largely open. This is consistent with the low DNAPL matrix entry pressures observed in the experiments.

DNAPL Natural Attenuation in Fractured and Weathered Shale

A field facility at the Oak Ridge National Laboratory is serving as an extraordinary example of how natural attenuation processes are eliminating the off-site transport of chlorinated organics in a fractured shale bedrock. The field facility consist of a 35 m long transect of multilevel sampling wells that extend from a waste burial trench containing organic solvents to a seep exiting into a perennial stream. Data suggests that anaerobic degradation of TCE is occurring in the saprolite and the upper portion of the bedrock. TCE concentrations are highest in the portion of the plume closest to the waste trench and TCE daughter products 1,2 DCE and vinyl chloride are dominant further downgradient. Geochemical indicators are also consistent with biodegradation. The microbial communities present at the field site have been characterized with molecular microbiological methods and indicate several types of potentially biodegrading organisms. A series of laboratory experiments using TCE in microcosms and columns of undisturbed saprolite are currently underway to determine whether biodegradation can be reproduced and quantitatively evaluated in the laboratory.

Fractured Till Column Experiments

TCE entry experiments were carried out in years 1-3 of the project in a large undisturbed sample of clay till. The studies show that TCE can enter very small fractures (5 to 6 μm) at relatively low pressure heads (a few m's or less). They also confirmed that matrix diffusion plays an important role in controlling the rate of dissolution of TCE residuals in fractures, which largely dissolve within a month or two of the initial contaminant "spill".

Planned Activities

The planned activities for 2000 include:

1. Continue and complete laboratory scale studies of biodegradation of organic solvents in fractured shale saprolite and complete microbial characterization of contaminated and uncontaminated field/lab samples using conventional and molecular techniques to determine influence of contamination on microbial communities and to identify organisms capable of solvent biodegradation.
2. Complete writing of a series of 5 articles based on the DNAPL injections and biodegradation studies.
3. Preparation of funding proposals for related research (a proposal for EPA is in-prep.).

Publications, Theses and Abstracts

Peer-reviewed Manuscripts

O'Hara, S.K., B.L. Parker, P.R. Jorgensen and J.A. Cherry. Trichloroethene DNAPL flow and mass distribution in naturally fractured clay 1: Evidence of aperture variability. Water Resources Research, 36(1), 2000.

O'Hara, S.K. and B.L. Parker. Trichloroethene DNAPL flow and mass distribution in naturally fractured clay: 2. Matrix diffusion effects and NAPL phase disappearance. Water Resources Research, accepted with minor revisions.

Driese, S., C. Penfield, and L.D. McKay, Lithologic and pedogenic influences on porosity distribution and groundwater flow in fractured sedimentary saprolite: a new application of environmental sedimentology, J. Sedimentary Research, in-review.

M. Lenczewski, P.M. Jardine, L.D. McKay, et al., Field evidence of biodegradation of chlorinated organic solvents in fractured and weathered shales, Manuscript in preparation for submittal to J. of Contaminant Hydrology.

Cropper, S.C., and L.D. McKay, Comparison of air/water and DNAPL/water capillary pressure - saturation behavior in a fractured shale saprolite, Manuscript in preparation for submittal to J. Contaminant Hydrology.

Plus 2-3 other manuscripts in preparation.

Theses

O'Hara, S.K., Solvent DNAPL flow and matrix diffusion in natural fractured clay: A large column experiment, MS thesis, Univ. of Waterloo, Ontario, Canada, 1997.

Cropper, S.C., Experimental observations of capillary pressure - saturation drainage of air and DNAPL in fractured shale saprolite, MS Thesis, Univ. of Tennessee, Knoxville, TN, 1998.

Theses by M. Lenczewski and A. Pitner are in progress and should be completed in 2000.

Solvents-Related Web Sites

L. McKay, Univ. of Tennessee
http://web.utk.edu/~lmckay
P. Jardine, Oak Ridge National Laboratory
http://www.esd.ornl.gov/facilities/hydrology/WAG5/
J. Cherry & B. Parker, University of Waterloo
http://www.science.uwaterloo.ca/research_groups/ucsgrp/

Fast Flow in Unsaturated Coarse Sediments

Project ID: 70069

Tetsu K. Tokunaga, Lawrence Berkeley National Laboratory

Research Objectives

Although the problem of rapid contaminant migration through very coarse granular sediments is recognized, our understanding of this flow regime is still incomplete. Gaining improved understanding of unsaturated flow in coarse granular sediments is important for practical concerns. Effective remediation and management of contaminated coarse-grained sediments such as those found at the Hanford Site requires knowledge of unsaturated fast flow. A better understanding of the failure mode for natural and engineered capillary barriers is also needed. This research proposal was developed to improve our understanding of the physics of unsaturated flow in coarse- to very coarse-textured sediments, and through this meet practical needs related to contaminant transport in such vadose environments.

Unsaturated flow in very coarse sediments is a critical area for improving our basic understanding of vadose zone flow and transport because it contains important aspects that are beyond the realm predictable by classical Miller-Miller scaling analyses. In particular, very coarse-textured (>1 mm grain-size) media can sustain high flow rates at relatively low saturations, doing so via film flow rather than by flow through an interconnected network of saturated pores. Thus, the physics of fast flow processes in unsaturated very coarse media is fundamentally different from that traditionally recognized in finer textured sediments. Our general objectives are (i) to quantify the macroscopic hydraulic properties of very coarse textured sediments in the near-zero (-10 to 0 kPa) matric potential region, and (ii) determine the microscale basis for fast unsaturated flow. Through these macroscopic and microscale studies, we intend to develop appropriate scaling relations for unsaturated flow in coarse-granular sediments.

Research Progress and Implications

This report summarizes progress during the 5 months of our newly funded project. In pursuit of our research objectives, studies are being conducted to quantify macroscopic (column scale) and microscopic (grain-film scale) hydraulic properties and processes in coarse sands and gravels. In order to obtain results that are directly relevant to the DOE, we are focussing most of our efforts on sediments from the Hanford Site (Hanford formation, grain-sizes ranging from 0.1 to 50 mm). Tests of similar nature are being conducted on quartz sands and gravels for the purpose of obtaining more general results.

Our analyses of film flow in coarse sediments are showing that fast flow is stable only at near-zero matric potentials. This is a difficult energy region to study because of extreme changes in saturation and conductance that take place, especially in coarser textured media. Some of the established macroscopic methods for measuring unsaturated hydraulic properties of porous media are unsuitable for coarse-grain sediments because they require that variations in saturation over short vertical distances be negligible. As part of this project, we have developed two types of column methods that permit acquisition of saturation-potential-conductance relations that are well suited for coarse granular media. The first method is designed to provide saturation-potential-conductance information based on monitoring matric potential and saturation during a series of constant rate infiltration tests. The recent initial testing of this method on Hanford formation gravel was successful. The apparatus is being modified to permit more rapid measurements. The other type of column device will permit hydraulic characterization based on transient imbibition and drainage experiments.

Microscale tests of film flow have recently been started. These experiments build on our previous experience with film flow on roughened quartz glass surfaces that served as model rock fracture surfaces. The method relies on determining average water film thicknesses using x-ray fluorescence of a solute tracer. A Hanford gravel sample is placed in a small suction plate device, and scanned with a defocused synchrotron x-ray microbeam while equilibrating to selected boundary matric potentials. Important differences and complications introduced in the studies on Hanford gravel include a high matrix fluorescence background and greater surface roughness. The latter feature is important in permitting stable film flow, but also requires more measurements for proper characterization. These x-ray experiments are conducted at beamline X26A of the National Synchrotron Light Source (Brookhaven National Laboratory). Experiments were conducted in the 0 to –10 kPa matric potential range, with most tests in the 0 to –2 kPa region. This latter region is important because it permits fast film flow in larger, unsaturated pores.

The studies on Hanford sediments described above have only recently been started, but it is anticipated that measurements of film flow at near-zero matric potentials will reveal a previously unrecognized mechanism for fast, unsaturated flow in coarse sediments.

Planned Activities

The macroscopic and microscale studies described above will be continued on a range of grain sizes, in both well-sorted and mixed size distributions. The combined data set will permit testing of scaling laws relevant for unsaturated flow in coarse granular sediments. The microscale x-ray fluorescence experiments will continue in conjunction with microtopography measurements. The combined results of macroscopic and microscopic experiments will be used to develop a tested, consistent physical model of unsaturated flow in coarse sediments. Column experiments of well-sorted sediments, and further microscale measurements will be in progress for the remainder of FY2000. Studies on mixtures of grain sizes will be done during FY2001. Implications of these results on capillary barrier performance will be tested during FY 2002.

Acknowledgments

We thank Keith Olson and Andrew Mei of LBNL for technical support, and John Zachara, Robert Lenhard, Steve Smith, and Bruce Bjornstad of PNNL for samples of Hanford formation sediment.

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

Project ID: 70187

Philip D. Meyer, Pacific Northwest National Laboratory

Christopher J. Murray, Pacific Northwest National Laboratory
Mark L. Rockhold, Pacific Northwest National Laboratory
Marcel G. Schaap, U.S. Salinity Laboratory
Martinus Th. van Genuchten, U.S. Salinity Laboratory

Research Objectives

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

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

Research Progress and Implications

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

additional data needed for our analyses (soil hydraulic property measurements at the Sisson and Lu Site) have been collected.

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

Planned Activities

Core samples will be obtained from the Sisson and Lu Site upon completion of the Hanford Science and Technology Program experiment at the site. This activity is scheduled for the latter half of June. Samples will be analyzed at the U.S. Salinity Lab for water retention, unsaturated hydraulic conductivity, and physical properties. Sample analysis is anticipated to take approximately two months. The hydraulic properties are required for the scaling analysis used in the parameterization/conditional simulation approach. Data analysis will be conducted in collaboration with the Hanford Site researchers. Scaling and geostatistical analyses using the newly-obtained hydraulic data will be conducted by this project. These analyses will be initiated in August or September. The neural network analyses using the currently available Hanford Site data will continue. The additional data will be included in the analysis when it becomes available. The simulation activities to be conducted under this project will commence in FY01.

In-Situ Characterizations of Dense Non-Aqueous Phase Liquids Using Partitioning Tracers

Project ID: 55216

Dr. Gary A. Pope, The University of Texas at Austin

Akhil Datta Gupta, Texas A&M University
Richard E. Jackson, Duke Engineering Services, Inc.
Minquan Jin, Duke Engineering Services, Inc.

Research Progress and Implications

Major advances have been made during the past three years in our research on interwell partitioning tracers tests (PITTs). These advances include (1) progress on the inverse problem of how to estimate the three-dimensional distribution of NAPL in aquifers from the tracer data, (2) the first ever partitioning tracer experiments in dual porosity media, (3) the first modeling of partitioning tracers in dual porosity media (4) experiments with complex NAPLs such as coal tar, (5) the development of an accurate and simple method to predict partition coefficients using the equivalent alkane carbon number approach, (6) partitioning tracer experiments in large model aquifers with permeability layers, (7) the first ever analysis of partitioning tracer data to estimate the change in composition of a NAPL before and after remediation (8) the first ever analysis of partitioning tracer data after a field demonstration of surfactant foam to remediate NAPL and (9) experiments at elevated temperatures.

We have developed a new analytic approach that has several advantages over existing approaches for inversion of tracer data. First, the technique utilizes an extremely efficient three-dimensional multiphase streamline simulator as a forward model. Second, the parameter sensitivities are formulated in terms of one-dimensional integrals of analytic functions along the streamlines. Thus, the computation of sensitivities for all model parameters requires only a single simulation run to construct the velocity field and generate the streamlines. The inversion of tracer data is then performed using a two-step iterative linearization that involves first 'lining-up' the breakthrough times at the extraction wells and then matching the production history. Our approach follows from an analogy between streamlines and ray tracing in seismology. The inverse method is analogous to seismic waveform inversion and thus, allows us to utilize efficient methods from geophysical imaging.

In estimation of spatially distributed parameters such as permeability and DNAPL saturation, it has been recognized for a long time that data is never abundant enough to constraint the parameters uniquely. The new approach taken in this research is to recognize this fact from the beginning and to solve for an ensemble of solutions, each equally valid. The nonuniqueness issue is attacked from different perspectives. First, Genetic Algorithms (GAs), an efficient optimization search method, are used. GAs span the whole search space, act as a directed Monte-Carlo search and produces the initial set of valid solutions. Each solution is then refined using a classical gradient-based method. Second, the solutions are forced to be smooth in some sense by adding a penalty term to the objective function. Solutions showing unnatural variations of parameter values are thus penalized. Third, a cluster analysis is used to group together similar solutions. Characterization of the uncertainty of the solution, often overlooked, is treated fully through two approaches. They both involve the computation of the sensitivity matrix but extract different information from it. This approach is currently being tested on both realistic synthetic examples and field data from the saturated PITTs at Hill AFB and the unsaturated PITTs at Kirtland AFB.

The first ever partitioning tracer experiments were completed in dual-porosity rock. These studies are needed to understand the behavior of partitioning tracers in such media, to compare with flow and transport models, to select the best tracers and operating conditions, and ultimately to determine

the viability and applicability of partitioning tracer technology for characterizing nonaqueous phase liquid contamination in dual-porosity aquifers. The first experiment was done in a Berea sandstone with a single fracture with and without NAPL in the fracture. The results of these experiments clearly show the combined impacts of partitioning to the NAPL, fracture transport and matrix diffusion. To the best of our knowledge, no such experiments have been reported in the literature, so the experimental methodology, partitioning tracer technology and interpretation approach are all entirely new and must continue to be developed. A variety of other tracers with different diffusion coefficients and partition coefficients have been tested to start this process. An analytical model was used to interpret these partitioning tracer single-fracture studies. The model shows very good agreement with the laboratory results. The agreement indicates that the physical processes assumed in the model are similar to the actual processes occurring in the laboratory experiments. The understanding of these processes that we have gained is essential to continued development of partitioning tracer technology as applied to fractured aquifers. The first ever field-scale modeling is under way using UTCHEM, a simulator which includes the necessary features for modeling both tracer partitioning and dual-porosity tracer transport. These simulations are essential for our understanding of the relative importance of various parameters and characteristics for partitioning tracer test design in fractured media. Inspectional analysis has been used to determine the appropriate nondimensional scaling groups to aid in the understanding and generalization of our studies with fractured media.

Two vadose zone partitioning interwell tracer tests were completed at Kirtland Air Force Base to evaluate a radio frequency enhanced soil vapor extraction remediation technology. The remediation effort was a project of the Advanced Applied Technology Demonstration Facility. This effort was the first attempt to estimate the change in the composition of the NAPL after remediation. The Peng-Robinson equation-of-state was used to model the thermodynamic interaction between the hydrocarbons and the partitioning tracers. From this interaction, the compositional effects were determined. This is the first time that both the volume of NAPL removed from the soil and the change in composition of the remaining NAPL due to the remedial action have been simultaneously measured in a field demonstration. This work is relevant to the many field sites where the NAPL consists of a complex chemical mixture and where the remediation process causes large changes in its composition such as when the NAPL is heated as part of the remedial process.

Alcohol tracer partition coefficients for coal tar were measured and compared to similar values for several different NAPLs. Coal tar is a multicomponent dense, nonaqueous phase liquid (DNAPL) primarily composed of polycyclic aromatic hydrocarbons. Despite the great complexity of coal tar, the results show that the partition coefficients can be predicted using the equivalent alkane carbon number approach just as well as for simple NAPLs such as trichloroethylene and decane. We have also investigated other very complex NAPLs such as a fuel oil with very high viscosity and in all cases we have found that the equivalent alkane carbon number approach is useful for correlating the tracer partition coefficients.

The Migration and Entrapment of DNAPLs in Physically and Chemically Heterogeneous Porous Media

Project ID: 54680

Dr. Linda M. Abriola, The University of Michigan

Dr. Avery H. Demond, The University of Michigan

Research Objective

This document summarizes EMSP funded research designed to improve our understanding of and ability to simulate the influence of subsurface chemical heterogeneities on DNAPL flow and entrapment in the saturated zone. Specific project objectives include: (i) the quantification of DNAPL interfacial and hydraulic properties; (ii) development and assessment of constitutive hydraulic property and continuum based multiphase flow models; (iii) exploration of DNAPL migration and entrapment in heterogeneous systems at larger scales; and (iv) development of innovative remediation schemes.

Research Progress and Implications

A series of experiments has been conducted to explore the influence of representative surface-active agents, dodecylamine (DDA) and octanoic acid (OA), on interfacial properties in PCE-water-quartz systems. DDA and OA exhibit pH dependent acid-base speciation in aqueous solution, resulting in aqueous chemistry-dependent interfacial tension and/or wettability in these systems. When the neutral species of DDA (pH > 10.6) and OA (pH < 4.8) was dominant, minimal changes to interfacial properties were observed because of preferential partitioning of DDA and OA into the NAPL. In contrast, the cationic form of DDA (pH < 10.6) sorbed both to quartz and NAPL-water interface, altering the wettability from water-wet to neutral wettability and lowering the NAPL-water interfacial tension. The anionic form of OA (pH > 4.8) sorbed only to the NAPL-water interface, lowering the interfacial tension by as much as 50%.

Additional experiments were designed to examine the influence of organic acids on the wetting properties of solid surfaces of varying mineralogy. Bottle tests were used to assess the wettability behavior of soils composed of quartz, iron oxide coated quartz, aluminum oxide coated quartz, limestone ($CaCO_3$), and shale in the presence of a dyed mineral oil and various aqueous solutions (pH=6.5) of OA (the anionic form of OA dominates at pH=6.5). In the absence of OA, all of the soils except the shale were observed to be strongly water-wet; i.e., the shale was partially NAPL-wet. In contrast, in the presence of 0.1 M OA, only the quartz soil was water-wet; the soils composed of iron oxide coated quartz, aluminum oxide coated quartz, limestone, and shale were strongly NAPL-wet.

Experiments were conducted to explore the influence of solution chemistry of organic acids and bases on the capillary pressure relationship. The influence of OA and DDA concentration on the capillary pressure relationship for a tetrachloroethylene (PCE)-water-quartz system was examined and compared to previous results obtained for the same solutes in an o-xylene-water-quartz system. Despite the different properties of PCE and o-xylene, including polarity, aromaticity, density, and pure solvent interfacial tensions, the speciation, sorption and partitioning of the solutes were similar and influenced the capillary pressure relationship similarly. When the pH was above the pKa, OA is preferentially in an anionic form and, therefore, OA remains in the aqueous phase where it influences the interfacial tension to a greater extent. Hence, the capillary pressure at a particular aqueous phase saturation was observed to be lower at pH values above the pKa. A similar lack of dependence on the nature of the organic liquid phase was observed in the DDA-NAPL-water-quartz systems. In this

case, however, capillary pressure relations were affected by pH dependent changes in both interfacial tension and solid wettability.

Additional research efforts have focused on the determination and quantification of hydraulic property relations for synthetic fractional wettability porous medium (systems composed of known water- and organic-wet fractions), and for media having uniform, well-defined, solid surface chemistries (quartz, Fe oxide coated quartz, Al oxide coated quartz, limestone, and shale). Results indicate that the magnitude and shape of the capillary pressure curves are strongly dependent on the fractional wettability of the system. As the DNAPL-wet fraction of a soil increases, for a given saturation and saturation history, the DNAPL-water capillary pressure decreases, becoming negative at higher water saturations. In the absence of surface active organic compounds, most soils having identical grain size distributions but different solid surface chemistry produced similar capillary pressure relations. After exposure to a 0.1 M solution of OA (pH=6.5) followed by prolonged rinses with Milli-Q water (approximately 50 PV), the hydraulic properties for some of these soils exhibited a much more pronounced variation in wettability depending upon the soil's solid surface characteristics. Recall that wettability bottle test for these soils demonstrated that iron oxide coated quartz, aluminum oxide coated quartz, limestone, and shale were strongly NAPL-wet in the presence of 0.1 M OA and mineral oil. Additional measurements of hydraulic property relations for these soils in the presence of various OA concentrations are planned.

For the soils with well defined fractional wettability and solid surface chemistry, transient outflow measurements were undertaken with the automated setup that was used to determine capillary pressure relations. This transient information is currently being used to determine relative permeability relations according to history matching procedures. Due to the inability of previously developed multiphase models to handle the measured time dependent water and DNAPL pressure boundary conditions, a new one-dimensional multiphase flow simulator has been developed to solve the direct problem (simulation of outflow data). This simulator has been successfully coupled with a nonlinear least-squares fitting routine to solve the indirect problem (optimize hydraulic property model parameters to the outflow data).

Residual water and DNAPL saturations were also found to systematically vary as a function of fractional wettability. The magnitude of residual DNAPL saturations varied by 52 to 80% for the experimental sands as wettability was altered. The residual organic saturation in finer textured sands reached a minimum at intermediate wetting conditions, whereas residual saturations in coarser textured soils decreased asymptotically with increasing fraction of organic-wet sand. These observations were explained in terms of plausible interactions between NAPL films and ganglia, and surface area considerations. For media with NAPL-wet solids, an inverse correlation of residual organic saturation with grain size can be easily explained in terms of the relationship between increasing solid surface area and decreasing permeability.

The PI's have adapted a two-dimensional multiphase flow simulator to explore the influence of coupled physical and chemical heterogeneity on DNAPL migration and entrapment in the saturated zone. For reasonable ranges of wettability characteristics, simulations suggest that spatial variations in wettability can have a dramatic impact on DNAPL distributions. In physically homogeneous coarse textured systems, increasing the contact angle or organic-wet fraction of a soil produced a prolonged slow migration of the DNAPL, creating larger contaminated aquifer regions with lower organic saturations. In coupled physically and chemically heterogeneous systems, interfaces of capillary property contrast (soil texture or soil wettability) led to higher organic saturations, increased lateral spreading, and decreased depths of organic liquid infiltration.

Based upon findings from these numerical studies, experimental research has been initiated in two-dimensional sand boxes to explore the coupled influence of physical and chemical heterogeneity on DNAPL migration and entrapment. Subsurface wettability characteristics were demonstrated to have a dramatic influence on DNAPL migration and entrapment. DNAPL-wet layers were shown to behave as a very effective capillary barrier, retaining DNAPL and inhibiting its downward migration until the layer became saturated with DNAPL. Subsequent experimental studies with this setup were conducted to assess the ability of DNAPL-wet layers to contain mobilized DNAPL during surfactant flushing. Results from this study suggests that wettability alteration could be used in conjunction with other remediation schemes to improve their efficiency and performance. Hydraulic properties

of the soils utilized in the two-dimensional infiltration studies discussed above have been measured. This information, in conjunction with the developed multiphase simulator, is currently being used to assess the ability of this simulator to predict observed DNAPL infiltration and redistribution behavior. The sand box observations are also being used to further refine constitutive hydraulic property models and to explore scale-up issues in modeling multiphase systems.

Planned Activities

The project completion date for this grant is September 14, 2000. Research efforts that are currently underway were identified above. Upon completion of these studies, efforts will be directed towards data analysis and the writeup of research findings.

Information Access

Bradford, S. A., L. M. Abriola, and F. J. Leij. 1999. Multi-fluid hydraulic properties for fractional wettability porous media. In: *Characterization and Measurement of the Hydraulic Properties for Unsaturated Porous Media* (Editors, M.Th. van Genuchten, F.J. Leij and L. Wu), University of California, Riverside, (In press).

Bradford, S. A., and L. M. Abriola. 1998. Entrapment and dissolution of organic liquids in chemically heterogeneous porous media. In: *IAHS Publication no. 250, Groundwater Quality: Remediation and Protection*, Tubingen, Germany, pp. 167-172.

Bradford, S. A., L. M. Abriola, and K. M. Rathfelder. 1998a. Flow and entrapment of dense nonaqueous phase liquids in physically and chemically heterogeneous aquifer formations. *Adv. Water Res.*, 22:117-132.

Bradford, S. A., L. M. Abriola, and K. M. Rathfelder. 1998b. Simulated entrapment and dissolution of organic liquids in chemically heterogeneous porous media. In: *Enviromeet 98- Behavior and Remediation of Nonaqueous Phase Contaminants in the Subsurface* (Editors C.V. Chrysikopoulos, J. Bear, and T. C. Harmon), University of California, Irvine, pp. 7-16.

Bradford, S. A., L. M. Abriola, and F. J. Leij. 1997. Wettability effects on two- and three-fluid relative permeabilities. *J. Contam. Hydrol.*, 28, 171-191.

Demond, A.H., K.F. Hayes, D.L. Lord, F. Desai and A. Salehzadeh. 1999. Impact of organic compound chemistry on capillary pressure relationships of sands. In: *Characterization and Measurement of the Hydraulic Properties for Unsaturated Porous Media* (Editors, M.Th. van Genuchten, F.J. Leij and L. Wu) University of California, Riverside, (In press).

Lord, D.L. 1999. Influence of organic acid and base solution chemistry on interfacial andtransport properties of mixed wastes in the subsurface. Ph.D. dissertation. Department of Civil and Environmental Engineering, The University of Michigan, Ann Arbor, MI.

Lord, D.L., A.H. Demond, K.F. Hayes, and A. Salehzadeh. 1999. Effects of surfactant chemistry on interfacial tension, wettability, and capillary pressure in multiphase subsurface waste systems, *Transport in Porous Media*, in press.

Lord, D. L., K. F. Hayes, A. H. Demond, and A. Salehzadeh. 1999a. Influence of organic acid solution chemistry on subsurface transport properties. 1. Surface and interfacial tension. *Environ. Sci. Technol.*, 31, 2045-2051.

Lord, D. L., A. H. Demond, A. Salehzadeh, and K. F. Hayes. 1999b. Influence of organic acid solution chemistry on subsurface transport properties. 2. Capillary pressure-saturation. *Environ. Sci. Technol.*, 31, 2052-2058.

Web Sites

http://www-personal.engin.umich.edu/~abriola
http://www-personal.engin.umich.edu/~sbrad

On the Inclusion of the Interfacial Area Between Phases in the Physical and Mathematical Description of Subsurface Multiphase Flow

Project ID: 54576

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Andrew F. B. Tompson; Lawrence Livermore National Laboratory

Research Objective

The scientific motivation for conducting this research lies in an assessment of the current state of modeling in the subsurface, where "modeling" refers to any systematic framework used to gain understanding of a system. At present, subsurface modeling addresses only the phases present, and even there considers the modeling process to be an extension of single phase flow. The shortcoming of this approach is that the governing flow equations do not account for some of the important physical phenomena. Therefore accurate simulation is more of an art than a scientific exercise. Experimental and field programs designed to measure data in support of these equations may actually be seeking curve fitting coefficients rather than information characteristic of physical phenomena. By providing a more general framework, we can contribute to improving the knowledge base related to important processes in the subsurface. We are convinced that such an improvement can be gained only by integrating various approaches to describing subsurface problems. Here, we are assessing and implementing the extended description of system physics by the following procedures: i) development of equations of mass, momentum, and energy transport for phases, interfaces between phases, and the common lines where interfaces meet; ii) provision of a consistent thermodynamic framework at the core scale that accounts for the interaction among the system elements; iii) derivation of needed closure conditions that describe the dynamics of the geometric elements (volume fractions, interfacial areas per volume, and common line length per volume); iv) development of state equations for capillary pressure as a function of saturation and area densities based on lattice Boltzmann simulations; v) implementation of the lattice Boltzmann procedure to determine core scale parameters from simulations at the pore scale; vi) extension of numerical simulators to account for the physics of the interfacial and common line processes. Integration of these elements relies on fundamental scientific inquiry to improve assessment capabilities of the multiphase flow situation. This work will impact both the study of flow of organic phases introduced into the natural environment and the study of natural multiphase systems such as air-water interactions in the vadose zone.

Research Progress and Implications

This report summarizes progress after 3.4 years of our work. The underpinning of this work is the development of a set of core scale continuum equations. These equations have been derived and are reported in As its underpinning, this research requires a set of macroscale continuum equations. These equations have been derived and are contained in reference [1]. To complete the general forms of the equations, the entropy inequality is applied as in [2]. The problem of closure of the system of equations is complicated by the need for dynamic descriptions of the changes in the geometric variables. Insight into the needed relations is obtained from a variational analysis of the equilibrium conditions [3, 4]. We have been able to develop a consistent thermodynamic description of multiphase flow at the core scale and to identify and overcome the need for closure relations. Building on these results, we have obtained equations for the geometric quantities and are in the process of writing up this

information. Thus, we have a closed set of equations that accounts for the interfacial areas in a systematic manner. The mathematical and experimental complexities of our approaches need to be made accessible to those who might wish to apply our results. We have made a significant effort to transfer our technology through organization of a workshop [5], presentation of our work in a simplified form that emphasizes physical over mathematical considerations [6, 7]. We are also engaged in research directed at gaining insight into the parameters that arise in the theory and at relating those parameters to physical problems. The approach employed relies on lattice Boltzmann modeling and some results are provided in references [8-11].

The results that we have developed challenge current understanding and approaches to modeling hysteresis in multiphase flow. Addition of the area per volume as an independent variable has shown promise for elimination, or at least dramatic reduction, of hysteresis in the capillary pressure vs. saturation relationship. Furthermore, the area per volume is a crucial parameter for developing models of mass transfer between phases and biological processes occurring at phase interfaces. These results will provide improved description of remediation processes at contaminated sites.

Planned Activities

Although not reported in the publications, additional work has been initiated to develop a reduced set of the balance equations and closure relations for a simplified core-scale physical system. These will be used in the development of the continuum scale model and for the identification of constitutive parameters from the lattice model simulations.

Information Access

1. Gray, W. G., and S. M. Hassanizadeh, "Macroscale Continuum Mechanics for Multiphase Porous-media Flow Including Phases, Interfaces, Common Lines, and Common Points," *Advances in Water Resources*, Vol. 21, No. 4 (July, 1998) pp. 261-281.
2. Gray, W. G., "Thermodynamics and Constitutive Theory for Multiphase Porous-media Flow Considering Internal Geometric Constraints," Advances in Water Resources, Vol. 22, No. 5 (January, 1999) pp. 521-547.
3. Gray, W. G., "Macroscale Equilibrium Conditions for Two-Phase Flow in Porous Media," *International Journal of Multiphase Flow*, Vol. 26, No. 3 (March, 2000) pp. 467-501.
4. Gray, W. G., "Elements of a Systematic Procedure for the Derivation of Macroscale Conservation Equations for Multiphase Flow in Porous Media," in *Kinetic and Continuum Thermodynamical Approaches to Granular and Porous Media*, edited by K. Hutter and K. Wilmanski, CISM Courses and Lectures No. 400, International Centre for Mechanical Sciences, Springer-Verlag, Vienna (April, 1999), pp. 67-129.
5. Soll, W. E., W. G. Gray, D. R. Janecky, and A. F. B. Tompson. Meeting Report: Linking the Pore and Continuum Scales Through Theory, Modeling, and Experimentation. *EOS*, *Transactions, American Geophysical Union*, 78(44), Nov 4, 1997, p. 495
6. Muccino, J. C., W. G. Gray, and L. A. Ferrand, "Toward an Improved Understanding of Multiphase Flow in Porous Media," *Reviews of Geophysics*, Vol. 36, No. 3 (August, 1998) pp. 401-422.
7. Hassanizadeh, S. M., and W. G. Gray, "Basic Equations of Flow and Transport in Porous Media," in *Bioremediation: Principles and Practice, Volume I, Fundamentals and Applications*, edited by Subhas K. Sikdar and Robert L. Irvine, Technomic Publishing Company, Inc., (October, 1997), pp. 19-57.
8. Soll, W. E., W. G. Gray, and A. F. B. Tompson, "Influence of Wettability on Constitutive Relations and its Role in Upscaling," in *Computational Methods in Water Resources XII, Vol. 1* (edited by V. N. Burganos, G. P. Karatzas, A. C. Payatakes, C. A. Brebbia, W. G. Gray, and G. F. Pinder), Computational Mechanics Publications, Southampton (1998), pp. 413-420.
9. Hou, S., X. Shan, Q. Zou, G. D. Doolen, and W. E. Soll. Evaluation of Two Lattice Boltzmann Models for Multiphase Flow. *J. of Computational Physics*, 138 1997. pp. 695-713.
10. Hazlett, R. D., S. Y. Chen, and W. E. Soll. Wettability and Rate Effects on Immiscible Displacement: Lattice Boltzmann Simulation in Microtomographic Images of Reservoir Rocks. *J. of Petroleum Science and Engineering*, 20(3-4), Jun 1998. pp. 167-175.
11. Zhang, D., S.Y. Chen, R. Zhang, and W.E. Soll. Pore scale study of flow in porous media: scale dependency, REV, and statistical REV. *Geophys. Res. Lett*, In Press. Feb 2000.
12. Gray, W. G., and C. T. Miller, "Comment on 'Dynamics of Wetting Fronts in Porous Media' by I. Mitkov, D. M. Tartakovsky, and C. L. Winter," *Physical Review E* Vol. 61, No. 2 (February, 2000) pp. 2150-2151.

Fate and Transport of Radionuclides Beneath the Hanford Tank Farms: Unraveling Coupled Geochemical and Hydrological Processes in the Vadose Zone

Project ID: 70219

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Research Objectives

The overall goal of this research is to provide an improved understanding and predictive capability of coupled hydrological and geochemical mechanisms that are responsible for the accelerated migration of radionuclides in the vadose zone beneath the Hanford Tank Farms. The study is motivated by the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of multiple contaminants at the Hanford site. Our objectives are to (1) provide an improved understanding of how lithological discontinuities within the sediments influence the propensity for preferential flow and matrix diffusion at different water contents, (2) quantify the significance of downward vertical advection, lateral spreading, and physical nonequilibrium processes on radionuclide transport under variable hydrologic conditions, and (3) quantify the rates and mechanisms of ^{137}Cs, $^{235/238}$U, and ^{99}Tc interaction with the solid phase under various hydrodynamic conditions and to determine how physical heterogeneities (i.e. stratification, pore regime connectivity) influence the retardation and degree of geochemical nonequilibrium during contaminant transport.

This report summarizes 0.5 y of research for a 3 y project.

Research Progress and Implications

Our approach involves (1) field-relevant, long-term unsaturated flow and transport experiments in undisturbed Hanford sediments, (2) multiple tracer strategies for quantifying preferential flow and nonequilibrium mass transfer processes at various water contents, and (3) a variety of novel surface spectroscopic techniques to quantify the distribution and chemical environment of contaminants as a function of sediment lithology and water content.

After a long and tortuous battle, a special-use permit to extract core from the White Bluffs was granted by the DOE-RL cultural resources agency. The White Bluffs was an ideal location for extracting Upper Ringold and Plio-Pleistocene core material since the physical and geochemical characteristics of these formations is nearly identical to those beneath the 200 West Area of the Hanford tank farms. Sediments from the Hanford Formation were acquired from another location. A rotary coring apparatus using a diamond bit core barrel was fabricated and mounted onto a backhoe so that cores could be obtained at any angle within the various formations. Undisturbed cores (0.3m diam X 0.3 m length) were drilled parallel to lithological layering (horizontally into the formation) and perpendicular to lithology (vertically downward). The different core types will serve to quantify the significance of downward vertical advection versus lateral movement of contaminants due to tension-dependent anisotropy. In order to extract the cores from the formation, the annulus separating the formation from the core was filled with expandable foam and allowed to harden. The cores were

then carefully removed from the formation by hand excavation. The rigid foam material not only maintained the integrity of the cores, it also contained an impression of the various sediment layers from the surrounding porous media, including Fe-oxide staining patterns. Thus, it was possible to infer the distribution of flow paths and mineralogical heterogeneities within the cores. A total of eight cores were obtained; three from the Upper Ringold sands (two horizontal, one vertical), three from the Upper Ringold sandy silts (two horizontal, one vertical), one angled core that cross-cut the Upper Ringold sands and silts, and one Plio-Pleistocene core. Bulk samples were obtained from each formation types as well as from the Hanford formation at a different location. The various cores were transported back to ORNL, where they are currently being prepared for unsaturated flow and transport studies using a variety of nonreactive tracers and the contaminants of interest ^{137}Cs, $^{235/238}$U, and ^{99}Tc.

Using an unsaturated flow technique described by Jardine et al., the fate and transport of multiple nonreactive tracers (Br, pentafluorobenzoic acid, and PIPES) and reactive radionuclides ^{134}Cs, $^{95/99}$Tc, and $^{235/238}$U will be investigated at a variety of water contents reflective of a range of recharge rates common to the Hanford site. The choice of Cs, Tc, and U as target contaminants is based on investigations by Riley and Zachara, Serne et al., and Jones et al. indicating that these radionuclides are priority pollutants that have migrated into the vadose zone beneath the tank farms of Area 200. The long-lived nature of ^{99}Tc and $^{235/238}$U and the huge inventories of vadose zone ^{137}Cs are of particular concern since they represent a significant risk with regard to potential groundwater interception. Our proposed unsaturated flow technique allows for fate and transport investigations in select pore regimes thereby isolating hydrological and geochemical mechanisms that are operative at different water contents. Thus we can essentially duplicate conditions in the field. The macroscopic fate and transport experiments will be coupled with interfacial molecular techniques (x-ray computed tomography, x-ray absorption spectroscopy, hyperquenching fluorescence) that serve to quantify the distribution and chemical environment of the sorbed contaminant species. Knowledge of the reaction mechanisms will serve to enhance our predictive capability of the observed contaminant transport

Figure 1 Drilling technician Norm Farrow preparing to obtain an undisturbed column using the rotary coring apparatus equipped with a diamond bit core barrel which was mounted onto a backhoe so that cores could be obtained at any angle within the various formations.

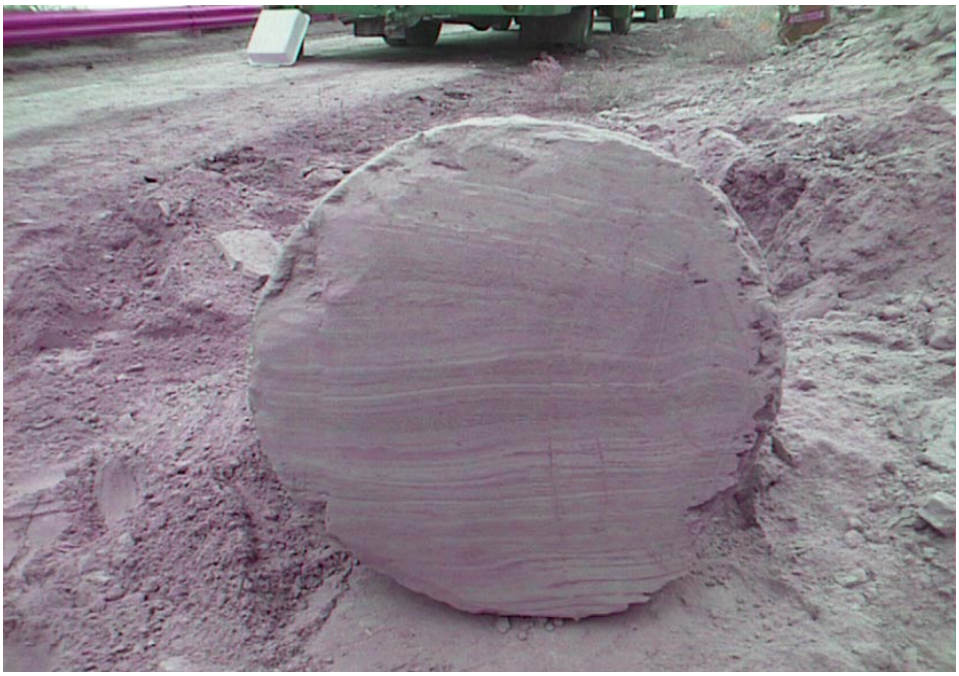

Figure 2 View of one end of an undisturbed core collected parallel to bedding planes from the Upper Ringold formation. Core dimensions are 0.3 meters diameter x 0.3 meters long. Heterogeneous distribution of iron rich layers are evident from the rust-colored bands. These mineralogical features are known to interact strongly with the contaminant metals and readionuclides in Hanford tank wastes.

experiments at the various hydrologic conditions. The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for Tank Farm restoration. By unraveling fundamental contaminant transport mechanisms in complex porous media, we will provide an improved conceptual understanding and predictive capability of a variety of vadose issues within the DOE system.

Physics of DNAPL Migration and Remediation in the Presence of Heterogeneities

Project ID: 55395

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Executive Summary

Spilled solvents have created pervasive groundwater contamination problems across the DOE complex because of their ubiquitous use, their toxicity and persistence in the environment, combined with the difficulty of recovering them from the subsurface. Because organic solvents are more dense than water and immiscible with water, they are commonly referred to as DNAPLs (dense non-aqueous phase liquids). They migrate below the water table downward and laterally under the influence of gravity, capillary, and viscous forces. Variations in media texture that the DNAPLs encounter as they migrate can have a profound influence on the migration path. This interplay between textural heterogeneities and driving forces complicates the migration of the DNAPLs and therefore it is not straightforward to predict the locations in the aquifer at which the spilled DNAPLs may ultimately reside. Uncertainties in the region of solvent contamination translate into higher remediation costs as the remedial system must be designed in light of these uncertainties. In an effort to clean up spilled DNAPLs, several remediation approaches are currently under development. Chemically enhanced solubilization, alcohol displacement, in situ oxidation, and air sparging are among the most promising. Many of these techniques have already undergone preliminary field demonstrations. However, results from such field demonstrations cannot be extrapolated to predict remedial performance under the wide range of field conditions to be encountered at spill sites across the DOE complex. Indeed, these techniques have not yet had the opportunity to be sufficiently tested and quantitatively compared in well-controlled laboratory experiments under heterogeneous conditions indicative of what can be expected in the field. In addition, the numerical simulation techniques used to predict DNAPL migration and remediation treatments have yet to be adequately verified through comparison against laboratory experiments conducted in heterogeneous media.

Research Objective

Our research effort has been designed as broad and crosscutting. The goal of our research is to develop a fundamental quantitative understanding of the role of physical heterogeneities on DNAPL migration and remediation in aquifers. Such understanding is critical to cost effectively identify the location of the subsurface zone of contamination and design remediation schemes focused on removing the source of the contamination, the DNAPL itself. There are two major aspects to the DNAPL problem: finding them (migration) and cleaning them up (remediation). We have been working on both. By designing lab experiments within heterogeneous porous media analogous to field conditions, we have been able to directly observe DNAPL initial migration and subsequent interactions between injected remedial agents and the DNAPL. In these experiments we have identified critical mechanisms having important implications affecting both the initial migration and the successfulness of remedial processes.

Research Progress and Implications

For migration, we have found the influence of heterogeneities to yield high DNAPL saturation "pools" of a wide range of sizes, corresponding to the effects imposed by textural variations between geologic facies. These pools are interconnected by fingers where very little DNAPL resides. When viscous forces are low, we discovered the DNAPL structure to pulsate at both the pore scale within fingers and at the unit scale within large pools due to a capillary-gravity pulsation mechanism. We have shown that this pulsation can lead multiple DNAPL migration pathways in time. We have built pore scale invasion mechanisms into a new modeling approach, a form of Modified Invasion Percolation or MIP model. Our simulations yield results that closely track the migration behavior seen in our experiments. Remediation experiments have shown both the successes and pitfalls of surfactants and in situ oxidation in the presence of even small pools. In the case of IFT lowering surfactants, a capillary bellows mechanism pushes DNAPL from the pool upstream into the flood where it then falls and can become caught within the lowest permeability units where it is bypassed by solubilization. For in situ oxidizers, DNAPL is not mobilized, however, the reaction product builds a low permeability rind around all the pools, isolating them from future oxidation. We also noted that the use of partitioning interwell tracer tests (PITT) to determine DNAPL saturations also has the potential to cause some mobilization of DNAPL from pools. As pools are expected at these and larger scales within any aquifer, such characterization and remediation methods must be used with caution.

From our research, we believe the following "products" and/or increased understanding to be of immediate and critical use to DOE DNAPL spill sites and cleanup efforts:

1. A fundamentally new and physically correct model (MIP) for DNAPL migration has been formulated, implemented and tested. This model can be extended to include the contact angle aging process found in mixed DNAPLs and combined with miscible transport codes to model DNAPL mobilization on IFT lowering and subsequent solubilization.
2. A series of length scales for DNAPL structure (i.e., pool height, finger diameter, and pulsation location) have been derived as a function of capillary, gravity and viscous forces within a heterogeneous media. These length scales can be combined to form the basis of a large scale structural growth model for DNAPL migration as well as the design of remediation applications.
3. The importance of heterogeneity to cause local saturations much higher than residual to be distributed throughout an aquifer has been clearly demonstrated. This multiple scale pool structure will largely control DNAPL migration extent and critically influence remediation attempts. Both DNAPL delineation before remediation and remediation design must be accomplished with this critical structure in mind.
4. Most importantly, *we emphasize caution and advocate a restrained approach to site remediation at this time.* Use of surfactants that cause excessive IFT reduction can cause the downward mobilization of the DNAPL and its penetration of low permeability layers. Such a scenario may have already happened at DOE site pilot tests Since full recovery of surfactant is never achieved, the migration of this fluid down gradient will continue to mobilize DNAPL far outside of the region where it was originally used. *Thus, all of these remediation approaches must be carefully considered prior to field implementation so that an existing contamination situation is not made worse.*

Planned Activities

We have found that liquid phase DNAPL movement in the context of heterogeneities, initially, during redistribution, and subsequently mobilized in the presence of characterization and remediation fluids is the critical determiner of remediation success or failure. Therefore, we now focus our research primarily on liquid phase movement in the context of heterogeneity and place lower priority on the consideration of DNAPL removal due to subsequent solubilization or oxidation. If during remediation, we can keep the DNAPL from mobilizing to undesirable locations, then we believe remediation schemes can be optimized to remove it. Therefore, we must understand and constrain mobilization within the heterogeneous system so that remediation can, "first do no harm." Since mobilization is brought on by IFT reduction (through the introduction of surfactants or alcohols) and since these

remain among the most promising remedial techniques, we will focus our primary research effort toward continued study of them. However, we will also begin to consider the issue of dirty or mixed DNAPLs and we will construct a demonstration experiment of air sparging in the context of heterogeneous aquifers.

Information Access (publications)

Manuscripts submitted for publication, pre-prints available from the PIs:

Glass, R.J., S.H. Conrad, and W. Peplinski, Gravity destabilized non-wetting phase invasion in macroheterogneous porous media: Experimental observations of invasion dynamics and scale analysis, in review August, 1999.

Glass, R.J., S.H. Conrad, and L. Yarrington, Gravity destabilized non-wetting phase invasion in macroheterogeneous porous media: Near pore scale macro modified invasion percolation model, in review November, 1999.

Zhong, L., A. Mayer, and R.J. Glass, Visualization of surfactant enhanced NAPL mobilization and solubilization in a two-dimensional micro-model, in review October, 1999.

Conrad, S.H., R.J. Glass, and W. Peplinski, Bench scale visualization experiments of DNAPL remediation processes in analog heterogeneous aquifers: Surfactant floods and in situ oxidation using permanganate, in review March, 2000.

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

Project ID: 70193

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Dr. John L. Wilson, New Mexico Institute of Mining and Technology
Dr. Michael J. Fayer, Pacific Northwest National Laboratory

Research Objectives

STCG # RL-SS29-S - Effect of Subsurface Heterogeneities on Chemical Reaction and Transport. Clastic dikes are vertically oriented subsurface heterogeneities that are common at the Hanford Site, including the subsurface sediments below the tank farms in the 200 West Area. Previous studies have suggested that clastic dikes may provide a fast path for transport of leaking fluid from the tanks through the vadose zone.

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

Research Progress and Implications

This report summarizes progress after the first 5 months of a 3-yr project. The major accomplishment thus far has been mapping the spatial distribution of clastic dikes over an area of about 60 sq km using aerial imagery and a GIS system. The mapping was performed over an area of the Hanford Site south of the Tank Farms where cultural features and sand dunes are not present, and thus do not obscure the pattern of the clastic dikes. Analysis of the map data produced thus far includes statistical analysis of the length and orientation of the clastic dikes. The mapping and analysis has revealed several important properties of the clastic dike network at the Site. The most important is the apparent presence of trends in the size of the clastic dikes. These trends will be used to guide the placement of transects where detailed data will be recorded in the field. Based on previous work it is believed that differences in the length of dikes may be related to their width, and possibly to the grain size of the material making up the dikes. If those relationships are found to exist, they will be used to predict the transport properties of the dikes in the area of the Tank Farms, based on identification of the length of the dikes using subsurface geophysical methods. A related activity that took place in conjunction with the Vadose Zone Advanced Characterization Workshop at the Hanford Site in January was the recording of ground penetrating radar (GPR) data by investigators from Lawrence Berkeley National Laboratory over several clastic dikes that had been identified by the project. This preliminary work suggests that GPR will be suitable for mapping the presence of clastic dikes that do not breach the ground surface.

Planned Activities

Fractal analysis of the existing GIS mapping data will be performed in March of 2000. Detailed field work at the Hanford Site, including geological and geophysical measurements (GPR) along transects selected from the GIS data will be performed in April through June of 2000. This field work will also include application of advanced characterization methods, air-minipermeametry and IR imaging, to examine the distribution of hydrogeological properties within clastic dikes. Data from the field work will be analyzed during the last quarter of FY00 and the first quarter of FY01 using geostatistical methods. In tandem with that analysis, field work will be planned for spring 2001, which will include a field scale infiltration experiment over a clastic dike. The experimental site will be characterized and monitored during the infiltration experiment using advanced geophysical methods (GPR, TDR [time domain reflectometry], and ERT [electrical resistance tomography]). Geostatistical methods will be used in FY01-02 to provide numerical 3-D grids of the infiltration site for flow and transport modeling, and the resulting transport models will then be compared with the actual observations during the transport experiments.

New Strategies for Designing Inexpensive but Selective Bioadsorbants for Environmental Pollutants: Selection of Specific Ligands & Their Cell Surface Expression

Project ID: 55185

Dr. Brent L. Iverson, University of Texas at Austin

Research Objective

Bacteria will be produced that have peptides or antibodies on the surface capable of binding toxic metal species with very high affinity. These bacteria will be used to make bioadsorbants, which will be characterized in detail.

Enzyme Engineering for Biodegradation of Chlorinated Organic Pollutants

Project ID: 55343

Dr. Peter G. Schultz, Lawrence Berkeley National Laboratory

Research Objectives

Halogenated organic compounds have had widespread use as fungicides, herbicides, insecticides, algaecides, plasticizers, solvents, hydraulic fluids, refrigerants and intermediates for chemical syntheses. As a result, they constitute one of the largest groups of environmental pollutants. Chlorinated organic compounds comprise the largest fraction of these materials, having been synthesized by large scale processes over the past few decades. Their ubiquitous use and distribution in our ecosystem has raised concern over their possible effects on public health and the environment.

The biodegradation potential of halogenated compounds is difficult and not well understood. Biological cleavage of carbon-halide bonds can be achieved by either enzymatic or biocatalytic dehalogenation or by spontaneous chemical dehalogenation of unstable intermediates. This research involves the protein engineering of existing enzymes and the "creation" of new enzymes (catalytic antibodies) with enhanced dechlorination capability for a wide variety of chlorinated organic pollutants. These enzymes could be used as such or could be inserted into microorganisms designed for high activity in contaminated environments.

Development of antibodies that catalyze the hydrolysis of halogenated aromatics will be carried out through a combination of chemical and genetic approaches. Haptens will be developed to generate antibodies that stabilize the transition state for hydrolysis of halogenated nitroaromatics. We will then randomize the variable regions of the antibodies and screen for antibodies with enhanced catalytic properties. If successful such an approach could be generalized and might allow one to tailor the specificity of a bioremediation catalyst for a given synthetic halogenated aromatic using the machinery of the immune system.

We will also attempt to clone, express, purify and to determine the structure and chemical mechanism of a known detoxifying enzyme, dechlorinating dehalogenase. In addition, knowledge gained from such studies will be used to redesign the dehalogenase for the purpose of expanding its biodegradative potential to include environmental pollutants that are currently non-biodegradable.

Characterization of Chemically Modified Hyperthermophilic Enzymes for Chemical Syntheses and Bioremediation Reactions

Project ID: 55033

Dr. Brian H. Davison, Oak Ridge National Laboratory

Michael Adams, University of Georgia

Research Objective

Remediation processes frequently involve species possessing limited solubility in water. We are interested in novel strategies that use molecularly modified enzymes with enhanced activity and stability for the remediation of recalcitrant compounds in organic solvents. The performance of naturally-occurring enzymes is usually quite limited in such organic environments. The primary objective of the current work is to gain a fundamental understanding of the molecular and catalytic properties of enzymes that have been chemically modified so that they are catalytically-active and chemically-stable in organic solvents. The premise for this study is that stabilized and activated enzymes, which can function at harsh chemical conditions, are optimally suited for bioremediation in nonaqueous media where substrates of interest are more soluble and processed with greater efficiency. This unique strategy is examined with respect to the degradation of chlorophenols and PCBs.

Research Progress and Implications

We are in the middle of the third year of a 3-year project, and this report summarizes work of the past year. We have obtained promising results both to demonstrate the proposed remediation strategy and to reveal fundamentals of the enzymatic catalysis in organic media. In one effort, ligninase (LiP) from *Phanerochaete chrysosporium* was modified with polyethylene glycol (PEG) and examined for the degradation of pentachlorophenol (PCP) in water-solvent mixtures. In another effort, basic catalytic behaviors of the chemically modified hyperthermophilic redox enzymes including ferredoxin, hydrogenase, and aldehyde oxidoreductase were examined in organic solvents.

I. PEG Modification of LiP and Its Bioremediation Applications

LiP was modified using PEG to enhance its activity and stability for the biodegradation of PCP in the presence of acetonitrile (MeCN). MALDI-TOF mass spectrometry analysis showed that the modified enzyme has one or two PEG groups attached to each protein molecule. The modified enzyme retained 100% of its activity in aqueous solutions and showed enhanced activity in the organic solvent. The activity of the modified enzyme was found to be over twice that of the native enzyme in the presence of 10% (v/v) MeCN. The solubility of PCP was enhanced significantly by the addition of MeCN to aqueous solutions. Capitalizing on the enhanced substrate solubility and the increased activity of the modified enzyme, the catalytic efficiency of the modified LiP in solutions containing 15% MeCN was over 11-fold higher than that of the native enzyme in aqueous solutions (from 44 to 480 mol PCP/mol LiP•h).

The degradation reaction products were examined. While tetrachlorobenzoquinone (TCBQ) was the only reaction product observed in previously reported papers, our work revealed the formation of three additional intermediates. This observation contributes to closing the mass balance between the yield of TCBQ and the disappearance of PCP. Furthermore, an additional product peak was observed

by HPLC when PEG-LiP, instead of the native enzyme, was used. This result implies that the chemical modification of enzymes may affect the reaction specificity.

II. Fundamentals of Modified Enzymes in Organic Solvents

Focus is on the basic properties of a hyperthermophilic redox protein, ferredoxin (Fd) from *Pyrococcus furiosus,* in organic solvents. This study will contribute to our knowledge of the oxidation and reduction chemistry of biocatalytic systems placed in nonaqueous reaction media.

Thermal stability: Studies were carried out with native and with PEG-modified Fd. Both enzymes dissolve in very polar organic solvents (e.g., DMSO) whereas PEG-Fd was also soluble in much less polar solvents including ethanol, propanol, butanol, benzene, and toluene. The thermal stability of both native and PEG-Fd is lower in DMSO compared to that in water ($t_{1/2}$ at 80°C of 60 and <10 min, respectively). Nevertheless, PEG-Fd showed better stability in organic solvents (the $t_{1/2}$ at 80°C increased to 30 min in toluene).

Redox Potential: The redox potentials of the native and PEG-Fds were determined using cyclic voltammetry. In general, little difference in redox potential was observed between the native and modified enzyme, either in aqueous solution or in solvents such as DMSO. This indicates that the integrity of the iron-sulfur cluster were not altered by PEG modification. However, organic solvent appeared to be capable of dramatically altering the redox potential of the protein. The redox potential of Fd was measured to be -690 mV in DMSO, which is much lower compared with that in aqueous solution (–390 mV at pH 8). Since the absorption spectra of the protein remained intact in DMSO, the dramatic shift in redox potential is most likely due to the changes in cluster environment rather than structural variations. This was verified using a mutant Fd, D14S, in which a cluster-ligating aspartate is replaced by serine. The ability to change cluster potential may prove useful in allowing the kinetics of electron transfer during catalysis to be altered depending on the solvent that is used.

Protein interactions in organic solvents: The effect of the PEG modification on the ability of Fd to accept electrons in organic solvents from another enzyme, aldehyde ferredoxin oxidoreductase (AOR), was investigated. Information from such a study should be helpful in designing multi-enzyme redox systems to degrade recalcitrant organic pollutants. AOR oxidizes aldehydes to acids and directly reduces Fd. While there was no activity in aqueous solution when either one of the two proteins was modified with PEG (PEG-AOR or PEG-Fd), remarkably, a high rate of catalysis (50% the activity of the native proteins) was observed when both proteins were modified. However, no activity was detected with the two PEG-proteins in toluene or ethanol.

Planned Activities

Since the project and subcontracts were initiated later than the official start date, a no-cost extension is requested. Accordingly, the following activities are underway:

1. PCB degradation using hyperthermophiles. Bacteria that grow near 100°C such as anaerobic heterotrophic archaeon, *Pyrococcus furiosus*, the anaerobic heterotrophic bacterium, *Thermotoga maritima*, and the aerophilic archaeon, *Pyrobaculum aerophilum* will be investigated. Our initial tests with crude cell extracts from these organisms failed to degrade PCBs (Aroclor 1242). In ongoing experiments the same organisms are being grown in the presence of PCB analogs to determine if the relevant enzymes can be induced or if intact and active cells are required for the degradation.
2. Membrane-bound enzymes for nonaqueous biocatalysis. Due to their highly hydrophobic nature, membrane-bound enzymes are expected to be soluble in organic solvents without any modification. We will focus on the hyperthermophile *P. furiosus,* It has been shown that its membranes contain high hydrogenase activity. Surprisingly, in contrast to the well characterized cytoplasmic hydrogenase, the membrane-bound enzyme did not reduce elemental sulfur. The enzyme has been solubilized using detergent (octyl-glucoside) and its purification is in progress. Its solubility, stability and activity in various organic solvents will then be determined.
3. Degradation of PAH's and DNAPLs with modified redox enzymes. Efforts are underway to conceive bioprocessing technologies using enzymes such as LiP or HRP for the in situ degradation of organic pollutants.

4. Modify the entire AOR-Fd complex with PEG (instead of modifying the proteins separately). This approach is expected to minimize the disrupting interactions between the AOR and Fd. Effects of water/solvent mixtures will be investigated.

Information Access

P. Wang, C. A. Woodward, E. N. Kaufman, "Poly(ethylene glycol)-modified ligninase enhances pentachlorophenol biodegradation in water-solvent mixtures," *Biotech. Bioeng*., 1999(in press)

C. Kim., C. A. Woodward, E. N. Kaufman, M. W. W. Adams, "Stability and sulfur reduction activity in organic media of hydrogenase from the hyperthermophilic Pyrococcus furiousus," *Biotech. Bioeng.*, 1999 (in press)

P. Wang, E. N. Kaufman, C. Kim., B. H. Davison, "Upon the oxidation reaction of pentachlorophenol catalyzed by ligninase in the presence of hydrogen peroxide*," Appl. Microbiology and Biotechnology*, 1999 (in preparation)

High Frequency Electromagnetic Impedance Imaging for Vadose Zone and Groundwater Characterization

Project ID: 70220

Gregory A. Newman, Sandia National Laboratories

David L. Alumbaugh, University of Wisconsin-Madison
G. Michael Hoversten, Lawrence Berkeley National Laboratory

Research Objective

Accurate description of transport pathways on the gross scale, the location of contamination, and characterization of heterogeneity within the vadose zone, are now realized as vital for proper treatment, confinement and stabilization of subsurface contamination at Department of Energy (DOE) waste sites. Electromagnetic (EM) methods are ideal for these tasks since they are directly sensitive to the amount of fluid present in porous media, as well as fluid composition. At many DOE sites it is necessary to employ lower frequency (<1 MHz) or diffusive electromagnetic fields because of the inability of ground penetrating radar (GPR) to penetrate to sufficient depths. The high frequency impedance method, which operated in the diffusive frequency range (10 Hz to 1 MHz), as well as the low end of the spectrum employed by GPR (1MHz – 10 MHz), is an ideal technique to delineate and map the aforementioned targets. The method has clearly shown the potential to provide needed information on variations in subsurface saturation due to local storage tanks and perched water zones, as well as mapping geological structures related to the subsurface hydrological properties and heterogeneity within the vadose zone.

Although it exhibits certain advantages over other EM methods, the impedance method comes with a set of assumptions and practices that can limit its potential. The first is the desire to locate receivers in the far-field of the transmitter which allows the use of magnetotelluric (MT) inversion codes to interpret the data. Unfortunately, one does not precisely know when one is in the far-field of the transmitter, because this depends on the geology we wish to image. The second limiting factor is the scarcity of complete 2D and 3D inversion schemes necessary to properly invert the data. While approximate 2D schemes are now emerging, rigorous 2D and 3D inversion codes are needed to bound the range of applicability of the approximate methods. We propose to address these problems in the following manner: (1) implement full non-linear 2D/3D inverse solutions that incorporate source coordinates and polarization characteristics, (2) use these solutions to study improvements in image resolution that can be obtained by making measurements in the near- and mid-field regimes using multiple source fields, (3) collect data at the Hanford Reservation with recently developed earth impedance measurement systems, and (4) interpret the field data with the newly developed inversion capability, as well as with additional and independent information such as well logs from boreholes. The benefit of this research to the DOE would be a combined measurement/interpretation package for non-invasive, high-resolution characterization of larger transport pathways, certain types of contamination, and heterogeneity within the vadose zone at the Hanford reservation, as well as other DOE facilities.

Research Progress and Implications

As of February 11, 2000, this report summarizes work for the first six months of the three year project. The project received initial funding in September of 1999. Over this period a prototype 3D inversion code has been developed for impedance data that incorporates source characteristics and coordinates. It is now undergoing further testing and development. A data set has been acquired by

Electromagnetic Instruments Incorporated (EMI) using the IMAGEM impedance field measurement system at the Richmond Field station in California. The purpose of this test data set is twofold. First, we need to analyze the data to insure the instrument is operating properly and consistently before its deployment at the Hanford reservation later this year for a three week survey. Second, the test data set provides a means to get the inversion programs under development, since the geology at the Richmond site is very well characterized. The inversion exercise will also provide feed back on instrument performance and the ultimate accuracy of the data it can deliver.

In January, a subcontract was placed with Dr. Michael Hoversten of Lawrence Berkeley National Laboratory to assist in the data interpretation and resolution issues of inverting mid- and near-field impedance data, and planning of the field surveys at the Hanford reservation. In late January a field site was selected at Hanford for our first three-week survey for the project. The site is clean (uncontaminated) and exhibits numerous clastic dikes that may be possible conduits for transporting of fluids and contaminants within the vadose zone. The goal of the survey is then to determine if we can image these dykes at depth.

Planned Activities

In the remaining first year of the project, we will complete a prototype version of a 2D-inversion code that also incorporates source characteristics coordinates. The 2D code will execute considerably faster than the 3D code, but assumes the geology is invariant along a preferred direction. Our first three-week field survey at Hanford will be carried over the clastic dike site later this spring using the IMAGEM field system. Preliminary analysis of the Hanford field data set will be carried out.

Seismic Surface-Wave Tomography of Waste Sites

Project ID: 55218

Leland Timothy Long, Georgia Institute of Technology

Research Objectives

The research objectives were to develop the computer programs and acquisition techniques for surface-wave group-velocity tomography and test these at three sites. Surface waves have many advantages for imaging the shear-wave structure in the near-surface, top 10 meters. The lack of robust analysis techniques has inhibited their application. The guiding objective of this project is to develop these techniques and make them available for application to environmental and waste site problems.

Research Progress and Implications

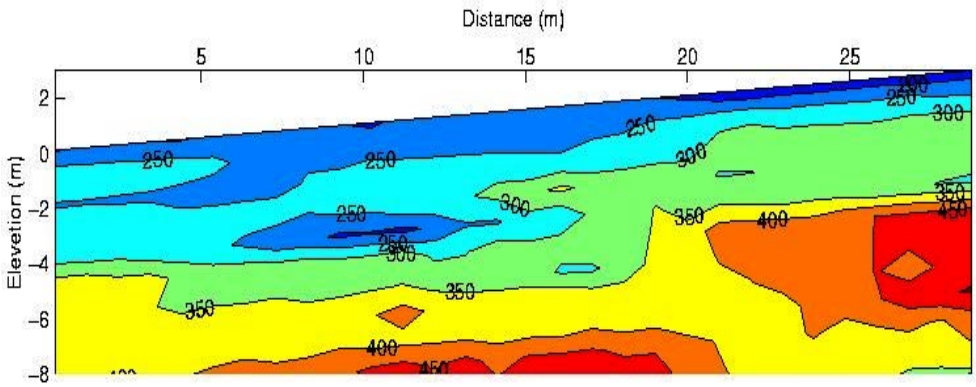
This report summarizes work after 3.5 years of a 3 year project with a one year unfunded extension. During the course of the work, we have developed computer programs to carry out the unique aspects of surface-wave group-velocity tomography. We believe that our computer programs and preliminary results demonstrate that useful data can be obtained using surface-wave group-velocity tomography.

In this project, we have applied the tomographic inversion of surface-wave velocities to areas with dimensions appropriate for near-surface structures that are often encountered in environmental problems. Surface-wave group-velocity tomography is made difficult by the complexities of the structure and by the indirect and computationally intensive techniques that are inherent in group-velocity interpretation. The advantages of tomography include, for example, the ability to image of shallow waste site structure from the site's periphery where access in not advised and the ability to reveal areas where trenches were used to dump wastes. The sensitivity of surface wave velocity to fluid saturation could allow surface-wave tomography to track fluid movement with time.

In order to compute the group velocities, we developed a damped and weighted least squares solution that is computationally a rigorous derivation and improvement to the simultaneous iterative reconstruction technique (SIRT). Four new data sets were obtained with a portable computer, and new acquisition programs written as part of this program. Additional programs were written to convert the acquired data to standard formats.

In the multiple filter technique, seismic data are filtered in the frequency domain. The group velocity for any given frequency is estimated from the arrival time of the peak instantaneous amplitude by our interactive visual program written using MATLAB. This program has been automated and tested with our current data. Arrival times that are found by the multiple filter technique must be corrected for group delays introduced by ground coupling of the instrument, instrument response, and source function. From the group arrival times, we obtained group velocity images at 1.0 Hz increments using the improved tomographic inversion method. Once the tomographic images are developed, dispersion curves for any position in the test area may be generated. These dispersion curves are then inverted for shear-wave structure. An example of a cross section of such interpretations is shown in the figure.

The results have two significant implications. First, the structures revealed in the figure have more detail than one could expect from traditional refraction methods, and at this shallow depth more detail than previously obtained using reflection methods. Second, we discovered conditions in the velocity structure that led to instabilities in the inversion for shear-wave structure. A related problem is that the inversion method assumes constant velocity layers, which are not good representations of the gradients observed in soils. Future studies should be directed to finding solutions that model the strong vertical gradients of real soil velocities.



Planned Activities

The work in the next 6 months will be directed toward completing the analysis of the Oak Ridge National Laboratory site data, which requires the development of a robust program to invert dispersion curves for shear-wave structure. These results will be made part of a paper describing the details of processing, analysis and structural interpretation of surface-wave group-velocity tomography. A paper on imaging near-surface buried structure with high-resolution surface-wave group-velocity tomography, which was submitted to the 2000 international conference on image processing, will be completed. With continued support during the next year, we will simultaneously 1) develop a robust inverse based of finite difference simulation of surface wave propagation in soils with velocity gradients and 2) obtain new data at 6 test sites to use in further testing and improving the analysis technique.

Publications

Long, L.T., and A. Kocaoglu (submitted September 1999) Surface-Wave Group-Velocity Tomography for Shallow Structures, Journal of Environmental and Engineering Geophysics,

Long, L.T.(1999). Seismic Surface Wave Tomography at Waste Sites, Research Note in: *Fast Times, The EEGS Newsletter*, February.

Long, L.T., and A. Kocaoglu, Processing Techniques for surface-wave group-velocity tomography, SEG Expanded Abstract, Annual Meeting, Calgary, Canada, August 2000.

Long, L. T., Kocaoglu, A. H., and Martin, J., Shallow S-wave structure can be interpreted from surface-wave group-velocity tomography, *in* Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems, Environmental and Engineering Geophysical Society, February, 2000 (SAGEEP00)

Long, L.T., A. Kocaoglu, W.E. Doll, X.Q. Chen, J. Martin. Surface-Wave Group-Velocity Tomography for shallow structures at a waste site, SEG Expanded Abstract, Annual Meeting, Houston, November 1-3, 1999.

Long, L.T., and Kocaoglu, A., (1999). Surface-Wave Group-Velocity Tomography for Shallow Structures, *in* Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems, Environmental and Engineering Geophysical Society, March, 1999 (SAGEEP99)

Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface

Project ID: 60115

Dr. Alan Levander, Rice University

William W. Symes, Rice University
C.A. Zelt, Rice University

Research Objective

Develop and test advanced near vertical to wide-angle seismic methods for structural imaging and material properties estimation of the shallow subsurface for environmental characterization efforts.

Research Progress and Implications

As of the middle of the second year of this three year grant we have pursued a number of research themes relevant to this proposal, including further processing and analysis on existing high resolution data, new data acquistion at an environmental remediation site, and data processing algorithm development.

We continued work on a multi-source high-resolution dataset acquired at an open pit copper mine in 1997. The data were acquired near the face of the mine wall, in order to match high frequency seismic structures to geologic outcrop and known fluid pathways in fracture zones in the mine wall. The datasets included surface reflection, surface refraction, and transmission refraction (mine rim to mine base). A paper describing the results of the data analysis on one of the 4 lines we acquired was submitted to Geophysics this spring (Akerberg et al., 1999), and results were presented at the 1998 SEG and 1998 AGU meetings (Processing continues on the additional 3 lines).

In August 1998 we conducted a high resolution survey at Hill Air Force Base, Utah, at an environmental remediation site. We chose this site for investigation because

1) It is an active remediation site, with a very shallow target depth (10-15m).
2) It has been drilled extensively, so that a general knowledge of the target zone is available.
3) Rice chemical engineers have conducted a Surfactant/Foam flood remediation effort at this site, and therefore have a good working knowledge of the site characteristics. (It was they who interested us in this site, as the characterization based on wells alone was inadequate for their remediation program).
4) The target is a paleo-channel cut in a clay layer that has been covered with alluvium. DNAPLs (TCE) have collected in the low spots in the paleo-channel. Although the extensive well field has outlined the paleo-channel, the details of the structure are not known well enough for the remediation efforts to remove all of the DNAPL.

The experiment was paid for by the AATDF program (DoD) and this DOE grant. We used 180 seismic channels from the PASSCAL program of IRIS (Incorporated Research Institutions for Seismology) and from Rice. We tested three different sources: an 8 gauge shotgun, a 0.22 caliber rifle, and an accelerated weight drop, which provided signals with frequencies from about 30 Hz to about 300 Hz. (Figure 1).

The data have been processed with conventional reflection processing and conventional refraction methods.

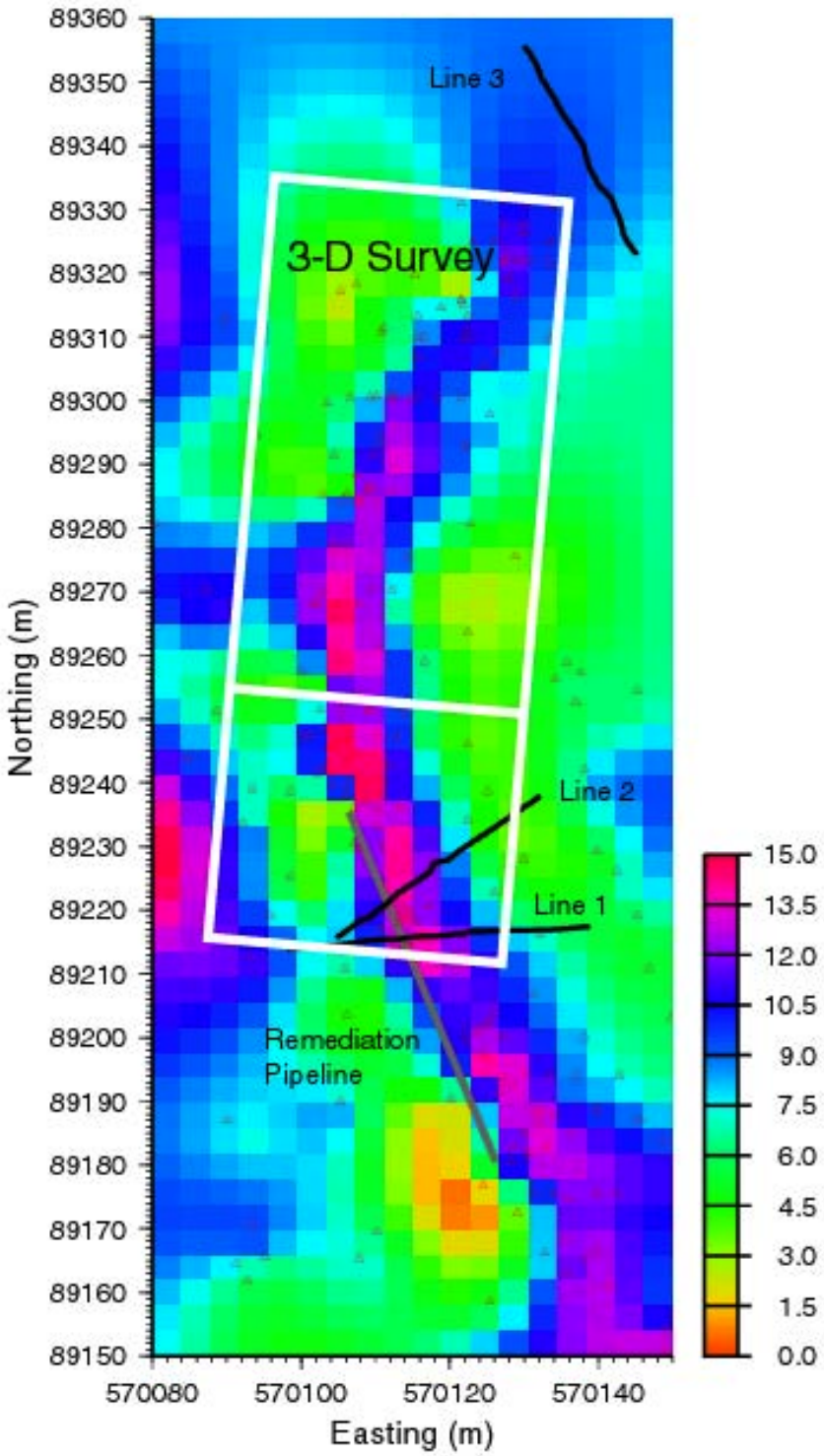


Figure 1: Map showing 1998 seismic lines at Hill AFB, the morphology of the channel from kriging well data, and the locations of the wells. The white box shows the 3D survey planned for 1999.

Reflection Images: Stacks of Lines 1 and 2 (Figures 2a and 2b) with minimal velocity analysis show that the paleo-channel changes morphology rapidly (compare lines 1 and 2). At present there are some ambiguities in subsurface definition due to velocity uncertainties. For example, on Line 2 there is evidence for a deeper reflecting horizon which mimics the shape of the event we have

Figure 2A: Line 1: Slide Hammer: Preliminary Stack

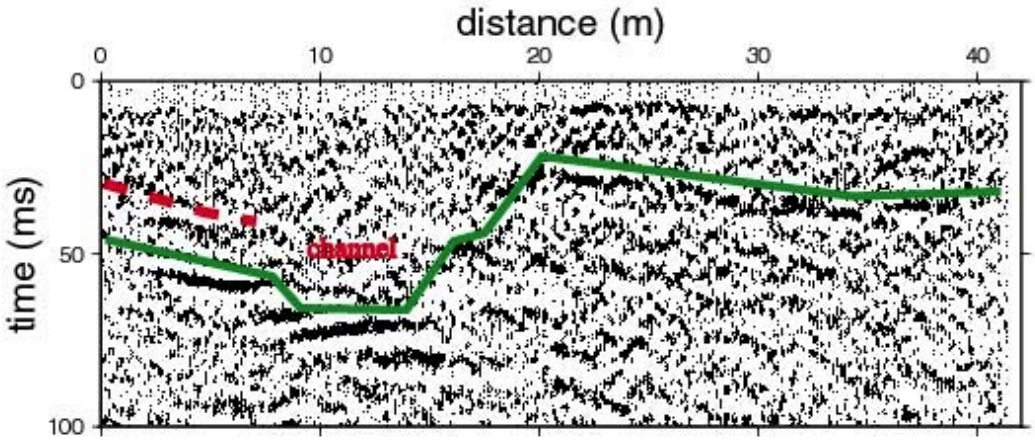


Figure 2B: Line 2: Slide Hammer: Preliminary Stack

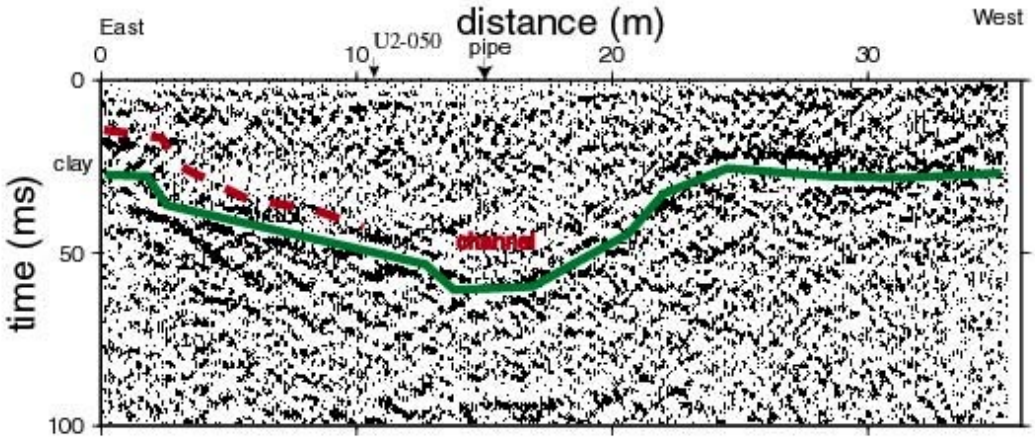


Figure 2: A) Preliminary stack and interpretation of Line 1 at Hill AFB (see Figure 1). B) Preliminary stack and interpretation of Line 2 at Hill AFB. Both lines show a clear channel structure, as well as deeper events. DNAPL's pool at the low spots in the channel. The two lines almost intersect at their western ends. The sections show a high degree of lateral variability in the channel structure.

tentatively identified as the paleo-channel. The deeper horizon may in fact be the water table, with the deeper horizon then being the top of the clay layer. Additional velocity analysis should clarify this point.

Refraction Analysis: The first arrival times from the Line 2 shotgun data have been picked and inverted for velocity and interface structure using a 2D travel-time inversion program that solves for the flattest (most laterally constant) model. A set of 9 different 2-layer models were derived that about equally well fit the data to within estimated uncertainties (2.5 ms). The boundary between the 2 layers is interpreted to be either the top of the water table or that between the Provo and Alpine formations; more velocity analysis of the refraction and reflection data in the near future will likely resolve this ambiguity.

The 9 models correspond to different a priori assumptions about certain features of the models that are not well constrained by the travel-time data or that can vary according to the data's constraint. The velocity in the near surface is less than the speed of sound, being between ~200-300 m/s. The velocity at the base of the first layer is poorly constrained by the data, but is likely between ~350-900 m/s. We have therefore derived 3 sets of models such that the velocity at the base of the first layer is either 350, 700 or 900 m/s (fixed). In each set there were 3 models determined: (1) a laterally varying velocity at the top of layers 1 and 2 was allowed; (2) a laterally varying velocity at the top of layer 1 was allowed but a velocity of 1500 m/s at the top of layer 2 was assumed; and (3) the best constant velocity was determined for the top of layer 1 (the surface) and a velocity of 1500 m/s at the top of layer 2 was assumed. A velocity of 1500 m/s was assumed for the top of layer 2 in 6 of the 9 models because of its likelihood of being the top of the water table.

The results show that the depth to the boundary between the surface layer and the top of either the water table or the clay layer has a well defined maximum located between 10-15 m from the east end of the line, at 6-11 m depth depending on the assumptions made concerning the seismic velocities as described above. This location and the maximum estimated depth (11 m) correspond closely to the assumed location of the paleo-channel based on available well data.

Model-Driven Waveform Inversion: Most of the effort on this part of the project over the past year falls into the "infrastructure" category. We have made significant progress in two areas, and have:

1) Implemented and tested on small and large problems a new method for imposing bounds on weighted mean squares of model parameters during inversion. This is a regularization method for linear and nonlinear inverse problems, following ideas put forward by D. D. Jackson and other geophysicists. The paper reporting this work is titled "Extremal regularization", and is available through the TRIP web site (http://www.trip.caam.rice.edu). It has been submitted for publication. The code is written in C++, and will be part of the next release of the Hilbert Class Library (HCL).
2) Revised and improved the methodology, announced in last year's report, for generating inversion applications from finite-difference/element simulators. This methodology has several components:

   A) An abstract class implementing the general finite difference loop: The user supplies an HCL operator class implementing the finite-difference step and sampling;
   B) Software to assist the user in transforming Fortran subroutines embodying the finite-difference stencil into the class code mentioned in A), without writing any C++ at all;
   C) An implementation of the adjoint state method, as part of the abstract class mentioned in A), which includes an essential checkpointing scheme due to Griewank rendering very large adjoint state computations feasible (10's of wavelengths for 3D viscoelastic finite-differences);
   D) A method for using so called Automatic Differentiation tools (in particular Ralf Giering's TAMC) to automatically generate the remaining Fortran modules needed to complete the inversion code, and "wrapping" them in appropriate C++, again without need for the user to write C++.

The code generating tools (B and D) have been tested on "naive" (non-C++-literate) users with success.

In addition, we have completely rebuilt the "SEGY" class on which all of the applications envisioned in this report will rely for I/O and vector algebra services, to take advantage of the improved features of HCL1.0. This class implements the SEGY data structure as an HCL vector class. It accommodates several other seismic data formats, including SU and SEP, and is designed to permit straightforward extension to yet others. The "SEGY" class will be released along with the rest of HCL1.0 at the end of the summer.

Planned Activities

We have a 3-D survey planned for Hill AFB in summer/fall 1999 as part of this project. Computer code integration and additional imaging software development are planned as well.

Information Access

Center for Computational Geophysics homepage:

http://terra.rice.edu/department/ccg/HAFB/

CCG members homepages:

http://terra.rice.edu/department/faculty/zelt
http://terra.rice.edu/department/faculty/levander
http://www.trip.caam.rice.edu/txt/bios/symes/william_symes.html
http://terra.rice.edu/department/staff/morozov
http://terra.rice.edu/department/students/dana

Papers

Zelt, C. A., Optimal utilization of sub-optimal 3D wide-angle data, Seis. Res. Lett., 70, 255, 1999.

Akerberg, P., D. Dana, A. Levander, T. Henstock, and C.A. Zelt, 1999, High resolution reflection surveying in an open pit copper mine, Tyrone, New Mexico, submitted to **Geophysics**, 8 March 1999.

Zelt, C. A., A. M. Hojka, E. R. Flueh, and K. D. McIntosh, 3D simultaneous seismic refraction and reflection tomography of wide-angle data from the central Chilean margin, Geophys. Res. Lett., in press, 1999.

Abstracts

P. Akerberg, D. Dana, A. Levander, C. Zelt, T. Henstock, 1998, High Resolution Shallow Seismic Imaging at an Open Pit Copper Mine, 10th Annual IRIS Workshop, 1998, Santa Cruz, CA.

D. Dana, P. Akerberg, A. Levander, C. Zelt and T.J. Henstock, 1998, Shallow-Seismic Investigation at an Open Pit Copper Mine: A Comparison with Drill Data, EOS, Trans. Am. Geophys. Union, 79, F652.

P. Passmore, G.R. Keller, K.C. Miller, A. Levander, G. McMechan, 1999, Single-channel recorder test results from two different active source experiments, Seism. Res. Letters, 70, 243.

D. Dana, C. Zelt, A. Levander, 1999, High-resolution seismic survey over a near-surface contamination site, submitted for the 1999 SEG International Exposition and Sixty-Ninth Annual Meeting.

C.A. Zelt, and A. M. Hojka, 3D simultaneous seismic refraction and reflection tomography of wide-angle traveltime data from the central Chilean margin, EOS, 79, F638, 1998.

D. Dana, P. Akerberg, C. Zelt, A. Levander, and T. Henstock, High resolution seismic imaging at a porphyry copper mine, Society of Exploration Geophysicists, New Orleans, LA, 1998.

Technical Reports

A. Levander, C. Zelt, D. Dana, Interim Report: Hill AFB OU-2 High-Resolution Seismic Study, Rice University Geophysics Program, 11 March 1999, submitted to HAFB and DOE.

Surface and Borehole Electromagnetic Imaging of Conducting Contaminant Plumes

Project ID: 55011

James G. Berryman, Lawrence Livermore National Laboratory

Research Objective

Electromagnetic induction tomography is a promising new tool for imaging electrical conductivity variations in the earth. The source field is a magnetic field generated by currents in wire coils. This source field is normally produced in one borehole, while the received signals are the measured small changes in magnetic field in another, distant borehole; however, the method may also be used successfully in combination with surface sources and receivers.

The goal of this procedure is to image electrical conductivity variations in the earth, much as x-ray tomography is used to image density variations through cross-sections of the body. Although field techniques have been developed and applied to collection of such EM data, the algorithms for inverting the magnetic data to produce the desired images of electrical conductivity have not kept pace. Prior to this project, the state of the art in electromagnetic data inversion was based on the Born approximation (requiring a low contrast assumption), or extensions. However, it is known that conductivity variations in fact range over several orders of magnitude and therefore require nonlinear analysis. The goal of this project has therefore been to join theory and experiment to produce enhanced images of electrically conducting fluids underground, allowing better localization of contaminants and improved planning strategies for the subsequent remediation efforts. The resulting field system can, after some more required work on calibration and reliability, be applied directly to EM characterization and remediation problems.

Research Progress and Implications

Project #55011 consisted of three major activities, with the major goal of developing EMIT into a mature field tool for environmental imaging applications:

(1) Development of an electromagnetic forward modeling capability in the appropriate frequency range (1-20 kHz) at LLNL for the first time.
(2) Development of a new electromagnetic data inversion method at LLNL and Stanford for the first time.
(3) Further development and upgrading of the field capabilities for EMIT, as well as use of these capabilities at an appropriately chosen field site.

(1) Forward Modeling Capability

Our forward modeling efforts are summarized in papers by Champagne et al. (1999; 2000) and Berryman et al. (1999). The resulting code is a 3D finite-difference Fourier-domain code that has been extensively tested against analytical results and results obtained from other codes. We call the code FDFD because of its finite-difference Fourier-domain character. As will be mentioned again in the next subsection, our forward modeling capability had special requirements, because it needed not only to produce the forward predictions of electrical and magnetic fields for given source configuration, but also to provide a simple means of computing the adjoint operator that was to be used in our new inversion method. This requirement was met by the code FDFD summarized in the papers already mentioned. The forward modeling capability development was one of the major achievements of the first two years of the project.

(2) EMIT Data Inversion Methods

Our most recent work on data inversion has developed an "adjoint method" for inverting these data (Champagne et al., 1999; 2000; Berryman et al., 1999; Dorn et al., 1999), thereby allowing higher resolution and higher contrast images than were previously possible.

The paper by Dorn et al.(1999), which was recently published in Inverse Problems summarizes a major new direction for research on EMIT data inversion problems of the type required for this project. The forward modeling efforts of Champagne et al. (1999; 2000) and Berryman et al. (1999) were critical for the development of the adjoint method because the adjoint method requires a method of computing the operator adjoint. Our forward modeling code was designed to make this set no harder than that of computing the forward result for the operator. The adjoint method of data inversion was one of the major achievements of the second and third years of the project.

We also have produced related work on electrical resistance/impedance imaging methods for high contrast media (Borcea et al., 1996; 1999) and on approaches to the analysis of both our own methods and those of others to quantify the attainable resolution in each situation (Berryman, 2000a,b).

(3) Field Work and Data Interpretation

Field equipment was acquired and assembled into a coherent data acquisition system for use by LLNL personnel for the first time. Some of our equipment was used by Berkeley students at the LLNL ACI site in both crosswell and surface-to-borehole tests and this project shared that data and the analysis of the data.

One field experiment was performed at Lost Hills, CA, in April, 1998, and the results were presented at SAGEEP by Buettner and Berryman (1999). At the Lost Hills site, steam had been injected into upper, middle, and lower zones of the Tulare formation since 1991 using injector 5035. More recently injector 5035 was refractured with steam, and service well O35 was completed as an injector for the middle and lower zones in order to increase the injection rate. The object of our monitoring was the shallow zone which extends from about 60 m to 85 m depth. Further details about the field site and the results may be found in the paper by Buettner and Berryman (1999) and in its references.

The data acquisition system integration and the field test were two of the major achievements of the first and second years of the project. Analysis of the field data using the new inversion methods will be one of the first items to be addressed in the renewal project if the renewal proposal is successful.

Planned Activities

The project was completed, including a no cost extension of three months, at the end of December, 1999, so no further work is planned or contemplated at this time until new funding arrives. A renewal proposal was submitted March 15, 2000. If the proposal is successful, the renewal project will lead to a well tested and calibrated field system and imaging tool that can subsequently be applied directly to EM characterization and remediation problems.

Publications

Berryman, J. G., Analysis of approximate inverses in tomography. I. Resolution analysis of common inverses, Optimization and Engineering, to appear in Volume 1 No. 1, 2000a.

Berryman, J. G., Analysis of approximate inverses in tomography. II. Iterative inverses, Optimization and Engineering, submitted, currently under review, 2000b.

Berryman, J. G., N. J. Champagne, II, and H. M. Buettner, A 3D finite-difference frequency-domain code for electromagnetic induction tomography, in Proceedings of the Second International Symposium on Three-Dimensional Electromagnetics, Salt Lake City, Utah, October 26-29, 1999, pp. 57—62.

Borcea, L., J. G. Berryman, and G. C. Papanicolaou, High contrast impedance tomography, Inverse Problems, 12, 835-858, 1996.

Borcea, L., J. G. Berryman, and G. C. Papanicolaou, Matching pursuit for imaging high contrast conductive media, Inverse Problems, 15, 811-849, 1999.

Buettner, H. M., and J. G. Berryman, An electromagnetic induction tomography field experiment at Lost Hills, CA, in Proceedings of SAGEEP, Oakland, CA, March 14-18, 1999, pp. 663-672.

Champagne, N. J., II, J. G. Berryman, H. M. Buettner, J. B. Grant, and R. M. Sharpe, A finite-difference frequency-domain code for electromagnetic induction tomography, in Proceedings of SAGEEP, Oakland, CA, March 14—18, 1999, pp. 931—940.

Champagne, N. J., II, J. G. Berryman, H. M. Buettner, FDFD: A 3D finite-difference frequency-domain code for electromagnetic induction tomography, submitted to J. Computational Phys., currently under review for publication in 2000.

Dorn, O., H. Bertete-Aguirre, J. G. Berryman, and G. C. Papanicolaou, A nonlinear inversion method for 3D-electromagnetic imaging using adjoint fields, Inverse Problems, 15, 1523-1558, 1999.

Information Access

For more information on this project, please contact: James G. Berryman, Lawrence Livermore National Laboratory, P. O. Box 808 L-200, Livermore, CA 94551-9900 Phone: 925-423-2905

Material Property Estimation for Direct Detection of DNAPL Using Integrated Ground-Penetrating Radar Velocity, Imaging and Attribute Analysis

Project ID: 70052

John Bradford, University of Wyoming

Scott B. Smithson, University of Wyoming
W. Stephen Holbrook, University of Wyoming

Research Objectives

The focus of our work is direct detection of DNAPLs, specifically chlorinated solvents, via material property estimation from surface ground-penetrating radar (GPR) data. We combine sophisticated GPR processing methodology with quantitative attribute analysis and material property estimation to determine the location and extent of residual and/or pooled DNAPL in both the vadose and saturated zones. An important byproduct of our research is state-of-the-art imaging which allows us to pinpoint attribute anomalies, characterize stratigraphy, identify fracture zones, and locate buried objects. Implementation and verification of these methodologies will be a significant advance in GPR research and in meeting DOE's need for reliable in-situ characterization of DNAPL contamination. Specifically, the work is geared toward addressing six key issues that have been identified as critical technology needs, both at specific DOE sites, and on a complex wide basis. These include:

1) Determining spatial and depth distribution of DNAPL contamination
2) Characterizing in-situ physical properties of sediments
3) Locating preferred hydrologic pathways
4) Characterizing horizontal and vertical dimensions of contaminant plumes
5) Determining variation in plume geometry due to important geologic features
6) Providing innovative, low-cost characterization approaches to extending subsurface data

Many DNAPLs, including chlorinated solvents, have much lower dielectric permittivity and conductivity than water. A contrast in electric properties is induced when DNAPL displaces water in the sediment column resulting in an anomalous GPR signature. To directly identify zones of DNAPL contamination, we focus on three aspects of reflected wave behavior - propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Velocity analysis provides a direct estimate of dielectric permittivity, attenuation analysis is used to identify variations in conductivity, and AVO behavior is used to estimate the dielectric permittivity ratio at a reflecting boundary. Areas of anomalously low dielectric permittivity and low conductivity are identified as potential DNAPL source zones. Preliminary work, which included theoretical development, modeling, and test pit studies, was highly successful and illustrated significant potential for quantitative direct detection methodologies in identifying shallow DNAPL source zones. It is now necessary to determine the consistency with which we can predict the location of DNAPL source zones, what level of residual contamination can be detected, and how accurately we can predict contaminant concentration. To this end, the project has three primary objectives:

1) Develop a suite of methodologies for direct detection of DNAPLs from surface GPR data
2) Controlled field verification at well characterized, contaminated sites
3) Exploratory contaminant detection in a field setting to be verified through direct sampling

Field experiments for the project will be conducted at the Savannah River and Hanford sites, and five DOD sites (Dover AFB, DE; McClellan AFB, CA; Port Hueneme, CA; Wurtsmith AFB, MI; Hill AFB, UT).

Research Progress and Implications

This report summarizes work after six months of a three-year project. In January, 2000, we conducted a 2160 sq. ft., 3-D, multi-offset, GPR survey in the vicinity of the A-014 outfall of A/M Area (U) at the Savannah River Site. The survey was designed to encompass a newly discovered shallow DNAPL zone (- 20 ft) with little or no contamination near the edges and a strongly contaminated zone near the center. The contaminants are thought to consist primarily of PCE. Preliminary analysis (pre-stack depth migration velocity analysis) of a profile near the center of the 3-D patch indicates a high velocity (low dielectric permittivity) zone that may be associated with a DNAPL pool (Figure 1). Using a time average equation to calculate saturation values, the high velocity zone is consistent with 35 - 60% DNAPL concentration assuming 24 - 0 % air saturation respectively. The high velocity zone does not correlate directly with previous cone penetrometer tests (Jackson et al, 1999), is consistent with higher DNAPL concentration than indicated in the direct samples, and therefore may be associated with the primary source pool in the vicinity. Assuming analysis of the full dataset is consistent with the initial findings, the presence of a DNAPL pool will be verified through direct sampling. Identification of the primary source pool will aid significantly in the implementation of a remediation plan.

Additional work that has been completed to date includes integrating three-phase flow and GPR response modeling to simulate a controlled tetrachloroethylene (PCE) injection experiment which will be conducted at Dover AFB in June and July of 2000. Fluid concentrations output by the flow model are used to generate a dielectric permittivity model using a time average equation. The GPR response is then calculated using an 2-D, acoustic, finite difference scheme. The acoustic code is appropriate for modeling wavefield kinematics and amplitudes assuming zero conductivity. Modeling results are being used in experiment planning.

Planned Activities

In early May of 2000, we will conduct a two week field experiment in the 200 area at the Hanford site. The primary focus of the work will be DNAPL detection in the vicinity of the carbon tetrachloride crib. In June and July of 2000, we will conduct a controlled injection experiment at Dover AFB, DE. Fifty liters of PCE will be injected in both the vadose and saturated zones then monitored for 30 days. The experiment will provide the opportunity to test both direct detection methodologies and the predictive capabilities of three-phase flow modeling coupled with GPR response modeling. From November, 2000 to November, 2001, we will conduct field experiments at Hill AFB, UT, Wurtsmith AFB, MI, McClellan AFB, CA, and Port Hueneme, CA. Each experiment will last 10 -15 days and will be conducted over known NAPL source zones.

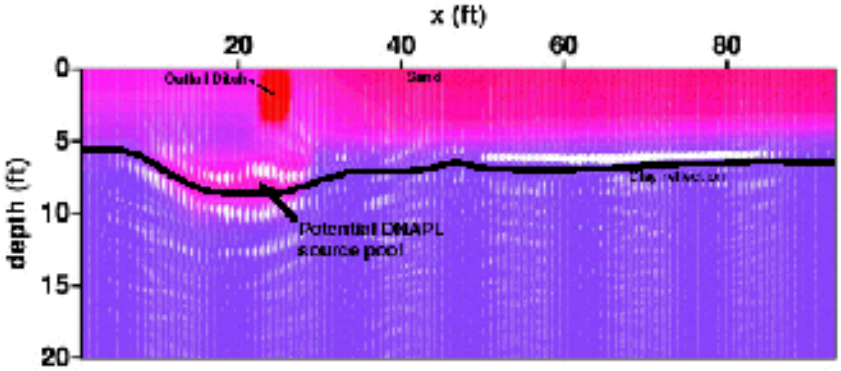


Figure 1 GPR velocity model and migration overlay for the Savannah River survey.

Reference

Jackson, D.G., Hyde, W.K., Rossabi, J., and Riha, B.D., 1999, Characterization activities to determine the extent of DNAPL in the vadose zone at the A-014 outfall of A/M Area (U): Technical Report WSRC-RP-99-00569, Westinghouse Savannah River Company, Aiken, SC.

3-D Spectral IP Imaging: Non-Invasive Characterization of Contaminant Plumes

Project ID: 55300

Dr. F. Dale Morgan, Massachusetts Institute of Technology

Research Progress and Implications

The Earth Resources Laboratory (ERL) performed a broad foundational study of spectral induced polarization (SIP) for site characterization. The project encompassed laboratory studies of microgeometry and chemistry effects on Induced Polarization (IP), an investigation of electromagnetic coupling (emc) noise, and development of 3D modeling and inversion codes. The major finding of the project is that emc noise presents a critical limitation for field implementation of SIP and conventional correction methods are inadequate. The project developed a frequency domain 3D complex resistivity modeling and inversion code

Laboratory experiments were conducted to study the effects of solution chemistry and microgeometry on the SIP response of sandstone. Results indicate that changes in chemistry affect the magnitude of the spectral IP response and changes in microgeometry affect the shape of the spectral IP response. The developed physiochemical IP model can be used to invert spectral IP data for an apparent grain size distribution.

Laboratory studies over the last twenty years have shown that SIP data must be acquired over several decades of frequency and include frequencies greater than 1kHz. A model of the components of emc noise has been developed and investigation with this model showed that inductive coupling is the most significant component. The study concluded that emc limits the frequency range of usable field data to approximately 100 Hz and below for typical site conditions. Several correction schemes have been developed based on treating emc as noise to be removed from the data, but our investigation has shown that these are not adequate for high frequencies, greater than 100Hz. Laboratory studies have demonstrated that the greatest response is the frequency range greater than 1KHz, hence the emc problem must be resolved for field implementation of SIP to advance.

The ERL developed 2D/3D time domain codes that perform inversions for chargeabilities based on schemes introduced by Siegel. The ERL has also developed a 3D complex resistivity code for inversion of frequency domain IP data. The algorithm accommodates a general earth model with a complex electrical resistivity as a function of frequency and 3-D spatial position. The forward problem is solved by the complex bi-conjugate gradient method, while the regularized inverse problem is solved by the nonlinear conjugate gradient method.

Time domain field data was acquired along a single survey line at the FS-12 plume, Massachusetts Military Reservation. The data was inverted with the developed 2D time domain code with the results having an excellent match to monitoring well data. The data was further analyzed by an innovative scheme where a “gross spectral chargeability” was determined from time domain data. The results show that there is valuable information in the spectra of the data.

Collaborative Research: Hydrogeological-Geophysical Methods for Subsurface Site Characterization

Project ID: 54655

Gary Mavko, Stanford University

Yoram Rubin, University of California
Frank Morrison, University of California
Jamie Rector, University of California

Research Objectives

The *significance* of this project is that it addresses the issue of site characterization: not only is this issue a very significant budget item in the site clean-up effort, but also it is now realized that accurate and reliable site characterization is the key to the success of any cleanup effort. Our *research objective* is to develop methodologies for inexpensive high resolution imaging of natural heterogeneities and for relating these heterogeneities to the hydrogeologic parameters that control flow and contaminant transport. Our focus is to help establish the scientific basis for applying shallow geophysics to hydrogeological problems, through sediment-rock physics. This includes identifying uncertainties in applying shallow geophysics interpretations to hydrogeological site characterization. The report summarizes work done since Spring 1999 related to the basic rock physics component of the project.

The objective of reservoir and aquifer characterization is to develop 3-D maps of flow properties so that fluid flow can be modeled. Historically, the petroleum industry has used geophysical data to predict flow properties and develop such maps. Recently, attempts have been made to adapt the same techniques to shallow aquifer environments.

Research Progress and Implications

In this report, we present a method for bounding the relationship between formation resistivity factor F and compressional velocity V_p. This method constrains porosity by constraining possible ranges of F-V_p data. Both the petroleum and environmental industries would benefit from this technique because of the potential for using electrical logs to better constrain seismic interpretations and develop more accurate maps of flow properties. Our approach is simple. It involves combining the well-known Hashin-Shtrikman bounds for electrical conductivity and acoustic velocity and tracking porosity changes with the bounds. The significance of our approach is in its potential for using known relationships between formation factor and material properties in sediments and rocks to explain velocity trends and vice versa. We found that $F - \phi$ data in unconsolidated glass beads, and suspensions fall along the lower HS bound (Figure 1) and the $F - \phi$ values move up the lower HS bounds as a result of compaction and sorting while cementation moves the points away from the bound. Both resistivity and seismic velocity are significantly influenced by the same variables: pore structure (amount, texture and content), grain contacts (shape, sorting and cement degree and type) and clays (amount, type and distribution). Despite the complexity in the $F - \phi$ and $V_p - \phi$ relationships the electrical and acoustic Hashin-Shtrikman HS bounds can be combined at equal porosities to provide bounds on the $F - V_p$ relationship (Figure 2). The bold, solid line in Figure 2 represents the lower HS bounds and the curved, bold, dashed line represents the modified Voigt V_p upper bound. The vertical dashed line represents a suspension porosity limit. No $F - V_p$ data is feasible within the region marked by x's. Thus combining electrical and elastic data narrows the feasible region, constraining the possible sediment properties.

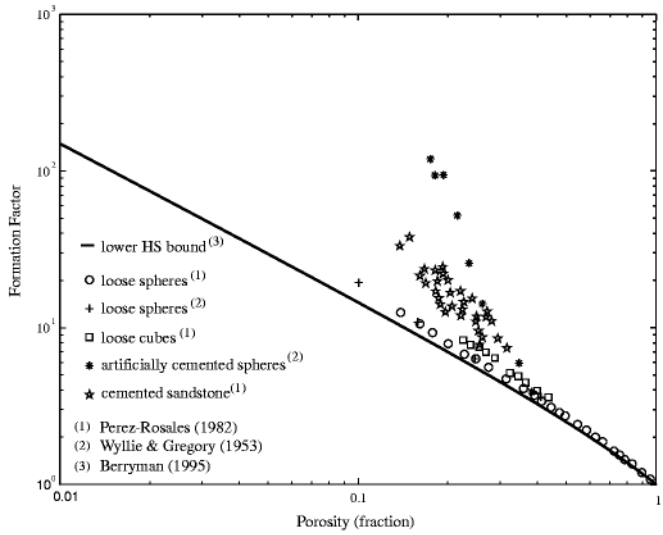


Figure 1

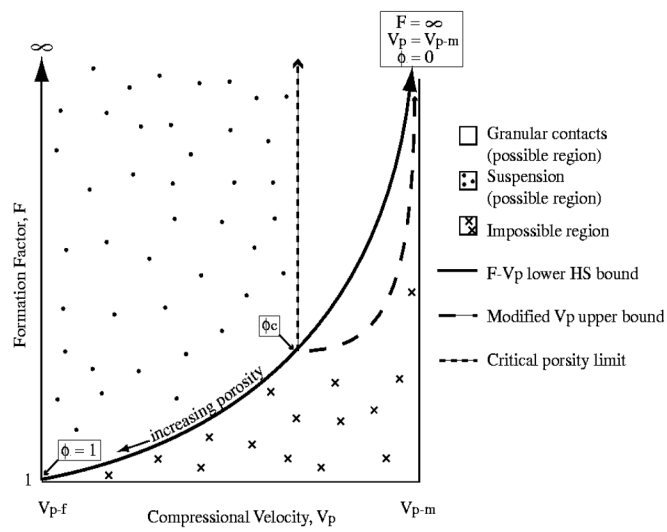


Figure 2

Planned Activities

The final planned activities in this project which concludes in March 2000 include preparation of reports and manuscripts for publication.

Information Access

This work was presented at the SAGEEP 2000 meeting. It will also be available at the web site: http://water.stanford.edu/doe/doeEMSP2000.html

Complex Electrical Resistivity for Monitoring DNAPL Contamination

Project ID: 70012

Stephen R. Brown, New England Research

David Lesmes and John Fourkas, Boston College

Research Objectives

Nearly all Department of Energy (DOE) facilities have landfills and buried waste areas. Of the various contaminants present at these sites, dense non-aqueous phase liquids (DNAPL) are particularly hard to locate and remove. There is an increasing need for external or non-invasive sensing techniques to locate DNAPL's in the subsurface and to track their spread and monitor their breakdown or removal by natural or engineered means.

Empirical studies suggest that distinct signatures of certain DNAPL pollutants can be identified by measuring the complex electrical resistivity of the contaminated soil. We propose to bring the field measurement of complex resistivity as a means of pollution characterization from the conceptual stage to practice. For this purpose we will document the detectability of clay-organic interactions with geophysical measurements in the laboratory, develop further understanding of the underlying physical and chemical mechanisms, and then apply these observations to develop field techniques to monitor the remediation of organic pollutants. This proposed work is driven by the following simple hypothesis: as organic compounds are removed (e.g., biodegraded or extracted through engineered remediation) the complex resistivity will change according to the new chemical make-up of the soil/groundwater system. Thus complex resistivity measurements can be used as an effective monitoring tool to indicate the progress of remediation activities.

Research Progress and Implications

This report summarizes work after 5 months of a 3-year project. A primary task of this work is to determine the magnitude and robustness of the effects of organic solvent contamination on the complex resistivity properties of soils. Therefore, we must first develop a measurement technique and carefully document its capabilities and reliability. To date we have designed and built a laboratory system (sample holder, electrodes, electronics, and data analysis software) for the measurement of the complex electrical resistivity properties of soil contaminated with organic solvents for frequencies in the range 0.02-10,000 Hz. Using resistor and brine standards we have been performing measurement accuracy, repeatability, and noise immunity tests of this system. At the present time we can safely resolve complex resistivity phase angle changes of about a milliradian over the entire frequency range. We are now prepared to try to reproduce the 100 milliradian phase angle anomalies in toluene contaminated clays presented by Sadowski and Olhoeft. We have also been performing an extensive literature search of complex resistivity phenomenon in soil systems. We now have in hand a theoretical framework for the effect of soil microgeometry parameters on frequency dependent resistivity to which we can compare our new results.

Planned Activities

- **Remainder of FY 2000:** Design and build a portable, benchtop, field usable complex resistivity system for contaminated soils. Begin laboratory parameter studies on idealized systems. Perform complex resistivity laboratory studies of baseline soil samples and samples contaminated by various organic solvents.

- **FY 2001:** Assess feasibility of field measurements: noise studies including baseline field noise test and sand box experiments. Collect data at a small-scale field site.
- **FY 2002:** Modeling: Analysis of laboratory data to identify distinguishing characteristics of complex resistivity contaminant signatures and develop algorithms to identify them. Use commercial resistivity inversion and imaging software to create images of subsurface distribution of contaminants from small-scale field tests.

Information Access

None at this time.

A Hydrologic-Geophysical Method for Characterizing Flow and Transport Processes Within the Vadose Zone

Project ID: 70267

Dr. David L. Alumbaugh, University of Wisconsin

Research Objective

The objective of this study is to analyze flow within the vadose zone during a mid-scale hydrologic test and to characterize transport processes in-situ. This project will employ numerical and experimental tools that have been developed under a previously funded EMSP proposal (project number 55332). Geophysical imaging techniques will be employed to image the changes produced by the transport experiments in-situ as they occur. Results will help to better understand flow and transport modes within the vadose zone at DOE sites, including the influence of natural heterogeneities and man-made structures. In addition the data will provide checks against which numerical flow and transport simulations can be compared.

Research Progress and Implications

As of the 6th month of a 36-month project, we are monitoring the progress of an infiltration experiment that was begun and continues under a previously funded EMSP project (see report on project 55332 for more information). We believe that the infiltration has reached steady state conditions and are in the process of validating both the geophysical imaging results as well as the various hydrologic measurements that have been made by collecting and analyzing subsurface samples. Students are being trained to operate the equipment and produce the geophysical images as those students that were involved in the first project have recently graduated. Two-dimensional (2D) and three-dimensional (3D) geologic models are being constructed using the geophysical images, well logs, and core samples that were collected prior to the infiltration beginning. These models will be later used to simulate the flow and transport experiments.

Planned Activities

In the near future we will begin simulating flow and transport experiments at the site using the models constructed from the preinfiltration data. These results will then be used to design a transport experiment, and modifications will be made on the infiltration system such that a salt tracer can be introduced simultaneously with the water that is producing the infiltration event. Modifications will be made to the geophysical imaging schemes such that they are optimized to image changes in the subsurface that occur due to the transport experiment. Once all modifications are complete, the transport experiment will be initiated, during which time geophysical and hydrologic data will be collected on a regular basis.

The Use of Dielectric and NMR Measurements To Determine the Pore-Scale Location of Organic Contaminants

Project ID: 54699

Dr. Rosemary Knight, University of British Columbia

Research Objective

A critical step in achieving the cost-effective treatment of a contaminated region of the subsurface is obtaining accurate information about the location and extent of subsurface contaminants. In many cases non-invasive means of subsurface characterization are required. This research addresses fundamental scientific issues that are central to the use and interpretation of dielectric and nuclear magnetic resonance (NMR) measurements as a means of detecting organic contaminants. We focus on the potential use of these methods to detect small amounts of adsorbed organic contaminants. The specific objective of our three-year research project was to investigate, through laboratory and theoretical studies, the effect of adsorbed organics on the dielectric and nuclear magnetic resonance (NMR) response of porous geological materials.

Research Progress and Implications

This report summarizes the work completed over the past 3.5 years of our project. Summarized below are the results of a series of studies designed to address our research objective.

Measurement of the Dielectric Constant

Laboratory measurements were made, in the frequency range 500 Hz to 10 MHz, of the dielectric constant of samples of sand and kaolinite clay; these sample were prepared with varying amounts of adsorbed oil and saturated with a 0.001 M NaCl brine. Previous research had suggested that the optimal way to determine the effect of adsorbed organics on dielectric measurements is to isolate the dielectric response of the "wetted" solid phase from the measured dielectric response of the total solid/fluid mixture; the "wetted" solid includes the response of the solid/fluid interface. Using an inclusion-based effective medium theory we were able to extract the dielectric response of the wetted solid from the experimental data. We found that the presence of sorbed oil had little effect on the dielectric response of the wetted sand matrix, presumably because of the very low surface area (0.2 m^2/g) of the solid/fluid interface. In contrast, the kaolinite (with a surface area of 5-12 m^2/g) data indicated a consistent decrease in the dielectric constant of the wetted solid phase as the amount of oil sorbed onto the solid surface was increased.

The results from this experimental study show that the presence of sorbed oil leads to a detectable change in the dielectric properties of saturated, high surface area geologic materials, and could lead to new ways of using dielectric measurements in the detection of contaminants.

Measurement of NMR Relaxation Times

Proton nuclear magnetic resonance (NMR) is a non-invasive technique that can be used in the laboratory or in the field to characterize porous geological materials. The NMR parameter of specific interest in our study is the measured relaxation time T of the water in the porous geological materials, which is described by the following equation: $1/T = 1/Tb + \rho\ S/V$, where Tb is the relaxation time of the bulk water, S/V is the surface area to volume ratio of the pore space, and ρ, the surface relaxivity, is a measure of the ability of the surface of the pore space to enhance the relaxation rate of the water

(1/T). Our working hypothesis throughout this study was that the presence of adsorbed organics would change the surface relaxivity (ρ).

An important first step in our research was to determine the influence of paramagnetic species, typically present in the near-surface environment, on NMR measurements. This issue was addressed through an extensive set of laboratory experiments in which we measured the NMR response of sands containing controlled amounts of paramagnetic Fe(III), present as adsorbed Fe^{3+} ions, solid Fe(III) oxyhydroxide surface coatings and separate Fe(III)-containing mineral grains. We found that each type of paramagnetic impurity had its own constant surface relaxivity and that the fraction of the sand surface populated with paramagnetic sites controlled the surface relaxivity of the sand. These results provide information about the effect of Fe(III) on NMR data that must be taken into account in order to accurately interpret NMR measurements in the near-surface environment. We anticipate that these results will be widely used as NMR is increasingly applied to address near-surface environmental problems.

To test our hypothesis that the adsorption of organic contaminants will affect the surface relaxivity of a geological material, we measured the NMR response of a water-saturated sand in its "clean" state and with various amount of adsorbed oil. For natural sand samples, with small concentrations of iron surface impurities, the surface relaxivity dropped sharply with increasing thickness of the adsorbed oil layer. We found that NMR could detect less than one complete monolayer of adsorbed crude oil (as little as 20 microgram/m^2) on silica gel if the silica surface was coated with a paramagnetic substance such as iron(III) oxyhydroxide; suggesting that NMR measurements could be a useful way of detecting trace amount of adsorbed organic contaminants.

Planned Activities

This project is in its final year; we received a one-year extension for the period September 1999 to September 2000. The next few months will be spent conducting a final set of experiments, completing our theoretical modeling, and submitting two papers for publication.

Information Access

Traci R. Bryar, Christopher J. Daughney and Rosemary J. Knight, Paramagnetic effects of iron(III) species on nuclear magnetic relaxation of fluids in porous media. Journal of Magnetic Resonance, **142**, 74-85 (2000). http://www.idealibrary.com/links/doi/10.1006/jmre.1999.1917

Christopher J. Daughney, Traci R. Bryar and Rosemary J. Knight, Detecting sorbed hydrocarbons in a porous medium using proton nuclear magnetic resonance. Environmental Science and Technology, **34**, 332-337 (2000). http://pubs.acs.org/reprint-request?es990637m/o72D

The Use of Radar Methods to Determine Moisture Content in the Vadose Zone

Project ID: 70115

Dr. Rosemary Knight, University of British Columbia

Research Objective

Moisture content is a critical parameter affecting both liquid-phase and vapor-phase contaminant transport in the vadose zone. Any attempt to model the behavior of a contaminant in the vadose zone, in order to design for the handling or remediation of a contaminated region, must adequately account for the spatial variation in moisture content. The variation in moisture content must therefore be determined with a high level of accuracy at the relevant scale or scales, given the governing transport processes. Traditional methods of drilling and direct sampling are very time consuming, limited in terms of spatial coverage, and have the associated risk of contacting and increasing the contaminated area. One solution is to use geophysical methods which can provide a high-resolution, non-invasive means of sampling or imaging the subsurface. Of specific interest in our research is the use of radar methods - both surface and borehole - as a means of determining *in situ* moisture content.

The objective of our three-year research project is to determine the optimal way to use radar methods to obtain information about moisture content in the vadose zone. In our research we will focus on two specific aspects of the link between radar images and moisture content. The first aspect or question we address is: Can we use a measure of the dielectric constant of a volume of the subsurface to determine the moisture content of that volume? The second question we address is involved specifically with the issue of spatial heterogeneity. Rather than using radar data to get estimates of moisture content at specific locations, can we use the radar data to directly obtain information about the way in which the level of moisture content varies spatially?

Research Progress and Implications

This report describes the progress that has been made in our research over the past six months.

Our first task has been to improve the clarity of radar images by correcting for frequency-dependent attenuation; this is responsible for wavelet dispersion, which is displayed in the radar image as a characteristic "blurriness" that increases with depth. Previous work by Turner and Siggins has shown that the electromagnetic (EM) wave attenuation parameter for many geologic materials is roughly linear with frequency over the bandwidth of a GPR wavelet, and thus the change in shape of a radar pulse can be described using one parameter, Q*, which is related to slope of this linear region. Assuming that all subsurface materials can be characterized by some Q* value, the problem of estimating and correcting for wavelet dispersion in GPR data becomes one of estimating Q* in the subsurface and deconvolving its effects through the use of an inverse-Q filter.

We tested our method by working with ground penetrating radar (GPR) data collected over an aquifer near Langley, British Columbia. To estimate Q* from these data, a number of traces across the GPR profile were analyzed using the wavelet transform. After converting the wavelet transform scale parameter into approximate frequencies, the centroid frequency at each point in time was calculated for the traces. Plots of this centroid value versus time show a distinct downward trend due to wavelet dispersion. Using a modified version of a technique developed for seismic attenuation tomography, the slopes of best fit lines through these plots were then used to determine a general value for Q* in the subsurface. Finally, an inverse-Q filter was applied to the data to yield a GPR image of significantly higher resolution than the original. Results indicate that this technique provides an effective means of estimating general values for Q* from surface-based GPR data. This technique

also has advantages over other methods of determining Q because it requires neither a reference spectrum nor the isolation of individual reflections.

The other focus of our current research is to determine how best to use and interpret the information contained in the radar data within a hydrogeologic framework. We have chosen to take a stochastic, rather than deterministic, viewpoint that allows for the incorporation of uncertainty in the measured radar parameters and in the petrophysical models that link the radar parameters to moisture content. We have identified three topics that have high priority and impact on the hydrological interpretation of radar data: i) the development and/or implementation of petrophysical models that relate the dielectric constant to water content; ii) the exploration of scale dependency of dielectric measurements in the subsurface and the consequences for hydrologic interpretation/modeling; iii) the application of methods for investigating statistically stationary and non-stationary systems using GPR. Petrophysical models relating water content and dielectric constant are generally dependent on the geometry of heterogeneity at the sub-measurement scale; as a means of choosing the appropriate model, we are exploring the use of anisotropy in the dielectric constant section obtained using cross-borehole tomography. We have also begun work addressing topics ii) and iii) above using GPR data sets, a variety of image sources and synthetic data. In particular, linear scaling relationships observed for the 1-D variograms are being extended and tested at higher dimensions using spectral methods.

Planned Activities

Over the next year, our focus will be on the development of petrophysical models for use in heterogeneous systems and on the continued examination of scaling phenomena in GPR data. In the summer/fall of 2000, both surface and borehole radar data will be acquired. With these new data sets, we will begin investigating the use of wavelet transforms on cross-borehole and surface GPR data for the detection and characterization of non-stationary systems based on hierarchical structures. We also plan to begin developing a model for the joint inversion of geophysical and hydrological data to determine hydrological parameters.

Enhancements to and Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument and Applications to Shallow Subsurface Imaging at Sites in the DOE Complex

Project ID: 60162

David L. Wright, U.S. Geological Survey

Weng Cho Chew, University of Illinois at Urbana-Champaign

Research Objective

The problems being addressed are those that require imaging of the shallow subsurface and include:

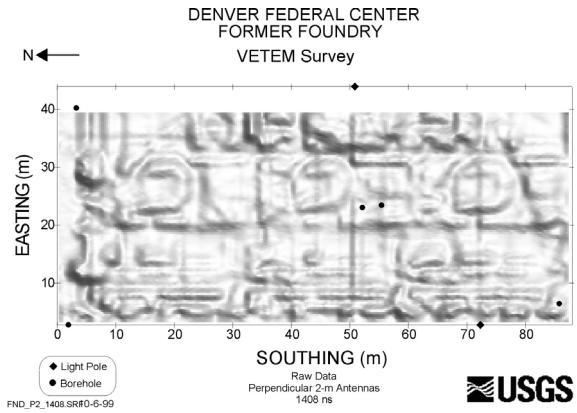
- Detection and Characterization of large metal and concrete structures.
- Improvement in the ability to characterize contaminant geological settings and predict the movement of contaminants in the vadose zone whether the dominant flow is matrix flow or fracture dominated.
- Improvements in the ability to image shallow subsurface leaks from waste pits or tanks.
- Improvements in the ability to detect and characterize buried objects in waste pits and delineate the boundaries of such pits.

The ability to more rapidly and accurately image the shallow subsurface in electrically conductive earth can result in considerable savings in time and money in environmental restoration or deactivation and decommissioning activites.

The objective of this research is to enhance the state-of-the-art in electromagnetic imaging of the shallow subsurface in electrically conductive media where ground-pentrating radar (GPR) provides insufficient penetration and time domain electromagnetic (TDEM) systems provide insufficient resolution. This objective is being pursued by instrumentation enhancements to the existing very early time electromagnetic (VETEM) system coupled with physical and numerical modeling. Success in this endeavor will improve the speed and accuracy of waste pit and trench location and characterization, and could have additional applications to shallow DNAPL and LNAPL spill and cleanup monitoring, clay barrier integrity assessment, and landfill stabilization monitoring. This could result in significant savings in time and money during characterization, remediation, and decommissioning of facilities.

Research Progress and Implications

This report summarizes work after 2.4 years of a 3-year project. We have made substantial progress on both the instrumentation and modeling and have done one demonstration at the INEEL Cold Test Pit, another at Pit 9, also at INEEL, and at the Denver Federal Center (DFC) over a buried WWII former munitions foundry. Accurate and rapid methods for modeling our antennas over conductive earth have been developed, and methods for calculating fields from buried conducting and dielectric objects have been obtained. 2D and 3D inverse methods have been investigated, and a fast 1D Distorted Born Iterative Method (DBIM) inversion algorithm has been successfully applied to VETEM field data from Pit 9 at INEEL and the DFC foundry site. The following figure is from the DFC foundry site.



VETEM images were better than any that have been produced by GPR or any of the commercial EM systems that have been used there to date.

Planned Activities

In the remaining months we plan to try a gradiometer configuration, begin moving to an All-Terrain-Vehicle towed version and finish documentation of the system. We also plan some additional calibration experiments.

Other Access to Information

1. W.C. Chew, "Imaging and inverse problems in electromagnetics," Advances in Computational Electrodynamics, Ed. A. Taflove, Artech House, Boston, pp. 653-702, 1998.
2. S.Y. Chen and W.C. Chew, "Electromagnetic subsurface remote sensing," in Wiley's Encyclopedia of Electrical and Electronics Engineering, editor, J.G. Webster, vol.6, pp.474-487, 1999.
3. T.J. Cui, W.C. Chew, A.A. Aydiner, S.Y. Chen, D.L. Wright, D.V. Smith, J.D. Abraham and R.T. Smith, "Nonlinear Inverse scattering of two-dimensional dielectric objects buried under a lossy earth," Research Report, Electromagnetics Laboratory, University of Illinois at Urbana-Champaign, No. CCEM-12-99, May 1999; also submitted to IEEE Trans. on Geoscience and Remote Sensing.
4. D. L. Wright, D. V. Smith and J. D. Abraham, "A VETEM survey of a former munitions foundry site at the Denver Federal Center", Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP2000), Arlington, VA, pp. 459-468, February 20-24, 2000.

Many additional papers in journals and conference proceedings such as GPR'98, SAGEEP'99. Also see the site http://empc22.ece.uiuc.edu.

High-Frequency Electromagnetic Impedance Measurements for Characterization, Monitoring, and Verification Efforts

Project ID: 60328

Ki Ha Lee, Lawrence Berkeley National Laboratory

Alex Becker, University of California

Research Objective

Specific DOE problems include 1) Maintaining physical integrity of clay caps to insure isolation of hazardous waste at the Savannah River Site (SRS), and 2) Lack of advanced vadose zone characterization geophysical techniques for adequately predicting the movement of contaminants in the Hanford and other DOE sites.

Non-invasive, high-resolution imaging of the shallow subsurface is needed for delineation of buried waste, detection of unexploded ordinance, verification and monitoring of containment structures, and other environmental applications. Electromagnetic measurements at frequencies between 1 and 100 MHz are important for such applications, because the induction number of many targets is small and the ability to determine the dielectric permittivity in addition to electrical conductivity of the subsurface is possible. Earlier workers were successful in developing systems for detecting anomalous areas, but no quantifiable information was accurately determined. For high-resolution imaging, accurate measurements are necessary so the field data can be mapped into the space of the subsurface parameters. We are developing a non-invasive method for accurately imaging the electrical conductivity and dielectric permittivity of the shallow subsurface using the plane wave impedance approach (Song et al., 1997). Electric and magnetic sensors are being tested in a known area against theoretical predictions, thereby insuring that the data collected with the high-frequency impedance (HFI) system will support high-resolution, multi-dimensional imaging techniques.

Research Progress and Implications

Following the initial sensor verification done last year for the frequency range of up to a few MHz, the project moved on to a wider portion of the radio spectrum up to 30 MHz to date. This step required development of a transmitter system in order to have signal at specified frequencies. Additionally, we have refined the behavior of the toroid sensor. On the data analysis part an inversion scheme for layered earth (1-D) has been developed, and the initial test using real data from Pt. Reyes appears successful.

Transmitter System: We acquired a function generator good to 30 MHz and an amplifier with a bandwidth of 250 kHz through 110 MHz. We also built and tested electric & magnetic transmitter antennae good through at least 30 MHz. To minimize spurious pickup and parasitic radiation, coaxial cables have been replaced by optical fibers. Additionally, we set up and tested a digital data acquisition system that operates under control of a notebook computer through a GPIB interface.

Field Measurements: In the initial development of the field system and its verification, measurements were made at the Richmond Field Station (RFS), University of California at Berkeley. The measured impedance showed good agreement with calculated values through 10 MHz. Conditions at the RFS are relatively conductive and, therefore, the electric field measurements are proportionately smaller and more difficult to make. Furthermore, the permittivity is relatively unimportant to the results. In a more resistive environment, such as the Savannah River Site clay caps, model studies

show that the electric fields are greater and that the field ratio is more sensitive to the subsurface permittivity. Two attempts at securing high-frequency impedance data in a resistive environment have been made to date. The first attempt was at Donner Summit in the Sierra Nevada Range using transverse and vertical magnetic dipole sources. Initial analyses show that the horizontal-mode impedance data agree well with a simple homogeneous earth model. The second attempt was made in a very highly resistive environment at Point Reyes National Seashore. Near surface resistivities of 2,000 to 10,000 ohm-m have been measured. Data from the survey and simple 1-D inversion results are shown below (Figure 1).

Toroid Electric Field Sensor(Lee, 1997): Improvements in the shielding and extraneous pickup problems with the prototype toroid have lead to an improved response. However, the sensitivity of the device to the ambient electric field needs to be further improved for practical use.

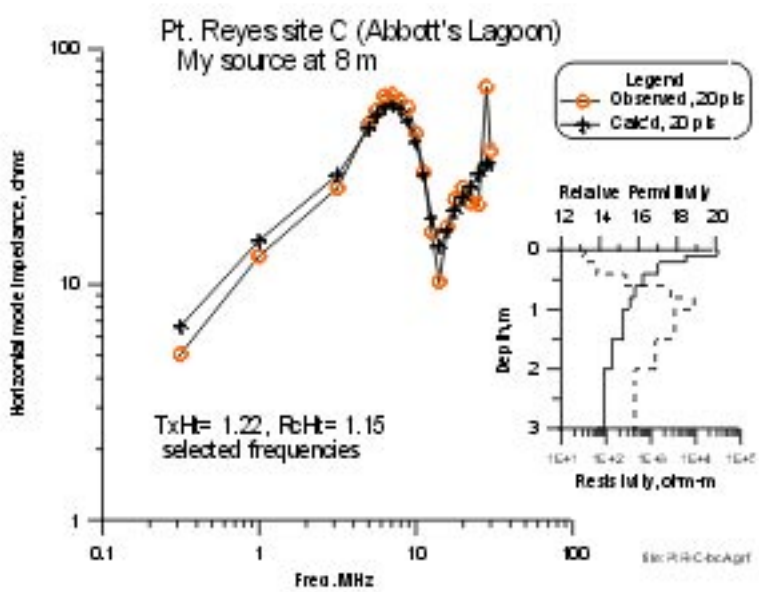


Figure 1. Impedance data (E_x/H_y) obtained at Pt. Reyes. 1-D inversion is shown on the right. Solid line is the resistivity, dotted line the relative permittivity.

Planned Activities

Future research will focus on cleaning up the signal measured by the stub dipoles and loop antenna through optical isolation and better signal conditioning. We will also investigate the phase calibration and stability of the system. We shall consider enhancing the toroid response amplitude through the use of a high-frequency ferrite core. An overall evaluation of the feasibility of the high-frequency impedance methods will be made as part of the final project report to DOE and the end users.

Information Access

Lee, K.H., 1997, High-frequency electric field measurement using a toroidal antenna, Lawrence Berkeley National Lab Report LBNL-39894, UC-2040.

Song, Y., Morrison, H.F., and Lee, K.H., 1997, High frequency electromagnetic impedance for subsurface imaging, Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP), 761-772.

Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions

Project ID: 70108

Patricia A. Berge, Lawrence Livermore National Laboratory

Brian P. Bonner, Lawrence Livermore National Laboratory
Jeffery J. Roberts, Lawrence Livermore National Laboratory
Dorthe Wildenschild, Lawrence Livermore National Laboratory

Research Objective

Our goal is to improve geophysical imaging of the vadose zone. We will achieve this goal by providing new methods to improve interpretation of field data. The purpose of this EMSP project is to develop relationships between laboratory measured geophysical properties and porosity, saturation, and fluid distribution, for partially saturated soils. Algorithms for relationships between soil composition, saturation, and geophysical measurements will provide new methods to interpret geophysical field data collected in the vadose zone at sites such as Hanford, WA.

Research Progress and Implications

This report summarizes work after 4 months of a 3-year project. We have modified a laboratory ultrasonics apparatus developed in a previous EMSP project (#55411) so that we can make velocity measurements for partially-saturated samples rather than fully-saturated or dry samples. We are testing the measurement apparatus using standard laboratory sand samples such as Ottawa sand samples. Preliminary results indicate that we can measure both compressional and shear velocities in these sand samples. We have requested Hanford soil samples (sands from split-spoon cores from an uncontaminated site) and expect to receive them in the next month. We have used the LLNL x-ray facility to perform x-ray computed tomography (XCT) imaging for several partially-saturated Ottawa sand and Lincoln sand samples. Preliminary results indicate that we can image amount and distribution of fluids in homogeneous sand samples. Continuing work from the previous EMSP project, we are testing a new data analysis method for seismic data that is expected to improve interpretation of seismic data from the vadose zone by showing how partial saturation affects seismic parameters. Our results suggest that the planned approach for this research is appropriate, that microstructure is an important factor for measured geophysical properties, and that seismic field experiments should be designed to collect both compressional and shear velocity data. The lead p.i. attended the EMSP Principal Investigator Orientation Meeting held in Richland, WA, in November and presented preliminary results at the Advanced Vadose Zone Characterization Workshop that was held in Richland, WA, in January.

Planned Activities

We plan to continue making laboratory measurements of compressional and shear velocities for partially saturated soils at low pressures, in the first two years of this project. We will also continue to make XCT images of partially saturated samples during the first two years of this project. In the second year, we will begin using rock physics theories and laboratory measurements to relate measured velocities to saturation and composition for soils. This work also will make use of results from a previous EMSP project (#55411) and other available geophysical data. In the second and third years

of the project, we will develop algorithms for relationships between composition, saturation, and geophysical measurements.

Information Access

The following publications are available at the URL http://www.llnl.gov/tid/lof/

Berge, P. A., 2000, EMSP Project 70108: Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions: *LLNL report UCRL-JC-137001-ABS,* submitted for presentation at the *Environmental Management Science Program (EMSP) National Workshop, sponsored by the DOE EMSP, to be held April 25-27, 2000, in Atlanta, Georgia.*

Berge, P. A., 2000, Powerpoint Presentation on EMSP Project 70108: Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions: *LLNL report UCRL-VG-137423,* presented at the *EMSP Principal Investigator Orientation Meeting, sponsored by EMSP and PNNL, held Nov. 16-18, 1999, in Richland, WA.*

Berge, P. A., 2000, Powerpoint Presentation on Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions: *LLNL report UCRL-VG-137423 rev. 1,* presented at the *Advanced Vadose Zone Characterization Workshop, sponsored by the PNNL Hanford Groundwater/Vadose Zone Integration Project, held Jan. 19-20, 2000, in Richland, WA.*

Berge, P. A., and Bertete-Aguirre, H., 1999, Laboratory velocity measurements used for inferring soil distributions from field seismic data (abstract): LLNL report UCRL-JC-135132-ABS, submitted to the 13th Annual Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP), to be held in Arlington, Virginia, February 20-24, 2000, sponsored by the Environmental and Engineering Geophysical Society.

Berge, P. A., and Bertete-Aguirre, H., 1999, Laboratory velocity measurements used for inferring soil distributions from field seismic data: LLNL report UCRL-JC-135132, submitted to the 13th Annual Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP), to be held in Arlington, Virginia, February 20-24, 2000, sponsored by the Environmental and Engineering Geophysical Society.

Berryman, J. G., Berge, P. A., and Bonner, B. P., 1999, Transformation of seismic velocity data to extract porosity and saturation values for rocks: LLNL report UCRL-JC-136703, submitted to the Journal of the Acoustical Society of America.

Bonner, B. P., Berge, P. A., Aracne-Ruddle, C. M., Bertete-Aguirre, H., Wildenschild, D., Trombino, C. N., and Hardy, E. D., 1999, Linear and nonlinear ultrasonic properties of granular soils (abstract): *LLNL report UCRL-JC-136207-ABS,* submitted to the *Materials Research Society Spring Meeting, to be held April 24-28, 2000, in San Francisco, CA.*

Wildenschild, D., J.J. Roberts and E. D. Carlberg, 1999, On the relationship between microstructure and electrical and hydraulic properties of sand-clay mixtures: LLNL report UCRL-ID-136122, submitted to Geophysical Research Letters.

This work was performed under the auspices of the U. S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

Joint Inversion of Geophysical Data for Site Characterization and Restoration Monitoring

Project ID: 55411

Dr. Patricia A. Berge, Lawrence Livermore National Laboratory

James G. Berryman, Lawrence Livermore National Laboratory
Jeffrey J. Roberts, Lawrence Livermore National Laboratory
M. J. Wilt, Lawrence Livermore National Laboratory

Research Objectives

Propose to develop a code for joint inversion of seismic and electrical data, to improve underground imaging for site characterization and remediation monitoring. Will invert the geophysical data to obtain direct estimates of porosity and saturation, rather than inverting for seismic velocity and electrical resistivity. In the first year, will perform laboratory measurements of elastic and electrical properties of sand-clay mixtures containing contaminants. Also will develop algorithms relating geophysical properties to porosity and saturation, using rock physics theories, geostatistical and empirical techniques, and available laboratory measurements. In the second year, will test the inversion code on available borehole log data to predict properties of cores. In the third year, will carry out a field experiment and invert the seismic and electrical data using the code.

Seismic-Reflection and Ground Penetrating Radar for Environmental Site Characterization

Project ID: 60199

Dr. Don W. Steeples, University of Kansas

Research Objectives

1. To examine the complementary site-characterization capabilities of modern, three-component shallow seismic reflection (SSR) techniques and ground-penetrating radar (GPR) methods at depths ranging from 2 to 8 m at an existing test site;
2. To demonstrate the usefulness of the two methods when used in concert to characterize, in three dimensions, the cone of depression of a pumping well that will serve as a proxy site for fluid-flow at an actual, polluted site;
3. To use the site as an outdoor mesoscale laboratory to validate existing three-dimensional ground-penetrating radar and seismic-reflection computer models developed at the University of Kansas.

To do this, seismic and GPR data are being collected along the same line(s) and within the same depth range. The principal investigators selected a site in central Kansas as a primary location, and although the site itself is not environmentally sensitive, the area offers attributes that are particularly useful for this research and allow the site to serve as a proxy for areas that are contaminated.

As part of an effort to evaluate the strengths of each method, the seismic and GPR surveys are repeated on a seasonal basis to establish how the complementary information obtained varies over time. Because the water table fluctuates seasonally at this site, variations in the two types of data over time also can be observed. Such noninvasive, in-situ methods of identifying and characterizing the hydrologic flow regimes at contaminated sites support the prospect of developing effective, cost-conscious cleanup strategies in the future.

Research Progress and Implications

The first field survey employing both methods was conducted in October of 1997, the second in March 1998, and additional experiments were performed in June, September, and November of 1998 and March of 1999. Additional GPR data were collected in July of 1999. One of our stated tasks is to reoccupy the same survey line on a quarterly basis for two years to examine changes in both the SSR data and the GPR data over time. Two factors drive such changes: First, soil-moisture conditions vary on a seasonal basis at the site. Secondly, the water table rises and falls about 1 m in response to changes in the level of the Arkansas River and in response to the presence of the many nearby irrigation wells.

At the test site, which is in the alluvial valley of the Arkansas River near Great Bend, Kansas, surface material consists of unconsolidated medium- to coarse-grained sand interspersed with clay stringers and clay lenses deposited by the Arkansas River. A hand-dug test pit about 10 m from the seismic line revealed the presence of a paleosol at a depth of about 0.6 m and cross-bedded sand descending to about 1.5 m. A coarser sand and gravel layer was found between 1.5 m and the water table. At the time of our seismic and GPR surveys, the water table was at depths of 1.7 to 2.8 m, based on measurements taken in a test well located 25 m from the seismic line. A well drilled about 40 m away from the seismic line encountered bedrock—a fine- to medium-grained Cretaceous-age sandstone—at a depth of 29 m.

Our experiments with GPR have included antennas with 110-, 225-, and 450-MHz center frequencies. Both common-offset and common-midpoint (CMP) surveys have been conducted. The CMP surveys greatly improved signal-to-noise ratio but did not increase significantly the depth from

which we were able to acquire interpretable data. Using GPR, we were able to image the water table at a depth of about 2 m; we found indications of stratigraphic variation along the line as well.

In the past, shallow seismic-reflection methods have been capable of imaging the subsurface from about 2 to 30 m. Modifying the field layout of the geophones and using an alternative seismic source have allowed us to image the subsurface from 0.6 to 2.1 m using seismic reflections. In our experiments, three distinct reflections within this range were observed while using surface sources and receivers at the test site in the Arkansas River valley. These were confirmed by 4th-order, finite-difference wave-equation modeling.

Our progress to date toward achieving workable ultrashallow seismic reflection imaging is largely attributable to an improved ability to measure the near-source wavefield. To accomplish this, we have collected data using a single 100-Hz geophone group interval of 5 cm. In contrast, typical "shallow" seismic surveys have receiver-group intervals of 1 m or more. Because we increased receiver coverage by a factor of 20 or more, our ability to delineate and improve the coherence of ultrashallow reflections over other interfering phases was enhanced. Seismic source energy was provided by a single shot from a .22-caliber rifle using subsonic, solid-point, short ammunition. The larger, more powerful shallow seismic exploration sources tested at the site (commercial seisguns and sledgehammers) generated enough near-field nonlinear deformation to make near-source (i. e., ultrashallow) reflection information undetectable.

Reports based on this work have been published in *Geophysics*, *Geophysical Research Letters* (GRL), the American Association of Petroleum Geologists' *Explorer* and other journals as listed. As of this writing, manuscripts have been submitted to the *Bulletin of the Seismological Society of America* (BSSA), *Geophysics*, the *Environmental and Engineering Geophysical Society Journal*, and *Geophysical Prospecting*. Abstracts have appeared in the expanded abstracts volume of the 1998 and 1999 Society of Exploration Geophysicists (SEG) meetings, and two additional abstracts have been submitted for the 2000 meeting. A poster session was presented at the American Geophysical Union's (AGU) annual meeting in San Francisco in 1998 and at the International Geoscience and Remote Sensing Society (IGARSS) June 1999 meeting in Hamburg, Germany.

Planned Activities

In the third year of this project, we are applying the combined seismic and GPR techniques to the characterization of the cone of depression of irrigation wells that will be pumping during this time. Data sets will be collected at each well prior to pumping, when equilibrium has been reached, and several weeks after pumping stops. The latter half of the third year will be used to finish processing data and to prepare manuscripts for publication.

Published Papers and Abstracts

Baker, G. S., C. Schmeissner, D. W. Steeples, and R. G. Plumb, 1999, Seismic reflections from depths of less than two meters: *Geophys. Res. Lett.*, **26**, 2, 279-282.

Baker, G. S., D. W. Steeples, and C. Schmeissner, 1999, In-situ, high-frequency *P*-Wave velocity measurements within 1 m of the Earth's surface: *Geophysics*, **64**, 2, 323-325.

Steeples, D. W., G. S. Baker, and C. Schmeissner, 1999, Toward the autojuggie: Planting 72 geophones in 2 seconds: *Geophys. Res. Lett.*, **26**, 8, 1085-1088.

Steeples, D. W., G. S. Baker, C. Schmeissner, and B. K. Macy, 1999, Geophones on a board: *Geophysics*, **64**, 3, 809-814.

Steeples, D. W., and Gregory S. Baker, 1998, Near-surface contributions to seismic static corrections: AAPG *Explorer*, **19** (June), 20-21, 29.

Dissertations and Theses

Baker, G. S., 1999, Seismic imaging shallower than three meters: Ph.D. dissertation, The University of Kansas, Lawrence, KS (May), 328p.

Pavlovic, Mario, 2000, Ground-penetrating radar in shallow aquifer detection and monitoring, Master's thesis, The University of Kansas, Lawrence, KS, May (in preparation).

Manuscripts Submitted, in Revision, or in Press

Baker, G. S., D. W. Steeples, C. Schmeissner, M. Pavlovic, and R. Plumb, "Improved vadose-zone imaging," submitted to *Geophysical Research Letters,* December 1999.

Baker, G. S., D. W. Steeples, and C. Schmeissner, "The effect of seasonal soil-moisture conditions on near-surface seismic reflection data quality," submitted to *Geophysical Prospecting,* October, 1999.

Baker, G. S., D. W. Steeples, C. Schmeissner, and K. T. Spikes, "Source-dependent frequency content of ultrashallow seismic reflection data," in press, *Bulletin of the Seismological Society of America,* 2000.

Baker, G. S., D. W. Steeples, C. Schmeissner, and K. T. Spikes, "Ultrashallow seismic reflection monitoring of seasonal fluctuations in the groundwater table," in revision, *Environmental and Engineering Geoscience Journal*.

Baker, G. S., D. W. Steeples, C. Schmeissner, and M. Pavlovic, "On coincident seismic and radar imaging," in revision, *Geophysics*.

Baker, G. S., C. A. McIntyre, L. A. Walczak and D. Steeples, "Improving ultrashallow seismic reflection data by reducing source energy," submitted to Expanded Abstracts, SEG 2000 International Exposition and 70th Annual Meeting, Calgary, Canada, in review.

Schmeissner, C., D. W. Steeples, Mario Pavlovic, Renato Prado, and Kyle Spikes, Recording seismic reflections using rigidly interconnected geophones: submitted to Expanded Abstracts, SEG 2000 International Exposition and 70th Annual Meeting, Calgary, Canada, in review.

Spikes, K. T., D. W. Steeples, C. Schmeissner, and R. Prado, Varying effective mass of geophones: submitted to Expanded Abstracts, SEG 2000 International Exposition and 70th Annual Meeting, Calgary, Canada, in review.

Published Abstracts

Baker, G. S., D. W. Steeples, and C. Schmeissner, 1999, On coincident seismic and radar imaging: Exp. Abst., SEG 1999 International Exposition and 69th Annual Meeting, Houston, TX, 484-487.

Baker, G. S., R. G. Plumb, D. W. Steeples, M. Pavlovic, and C. Schmeissner, 1998, Coincident GPR and ultrashallow seismic imaging in the Arkansas River Valley, Great Bend, Kansas: Exp. Abstr., SEG 1998 International Exposition and 68th Annual Meeting, New Orleans, 859-861.

Baker, G. S., D. W. Steeples, C. Schmeissner, and B. K. Macy, 1998, In-situ, high-resolution *P*-wave velocity measurements within 1 m of the Earth's surface: Exp. Abstr., SEG 1998 International Exposition and 68th Annual Meeting, New Orleans, 856-858.

Steeples, D. W., G. S. Baker, C. Schmeissner, and B. K. Macy, 1998, Geophones on a board: Exp. Abstr., SEG 1998 International Exposition and 68th Annual Meeting, New Orleans, 852-855.

Steeples, D. W., Baker, G. S., and C. Schmeissner, 1998, Toward the autojuggie: Planting 72 geophones in 2 seconds: Abstr., American Geophysical Union, 1998 Fall Meeting, Dec. 6-10, San Francisco, CA.

Plumb, R. G., D. W. Steeples, G. W. Baker, C. Schmeissner, and M. Pavlovic, 1999, A combined ground-penetrating radar and shallow seismic reflection approach to characterizing hydrological flow: International Geoscience and Remote Sensing Society (IGARSS) meeting, Hamburg, Germany, June.

A Hybrid Hydrologic-Geophysical Inverse Technique for the Assessment and Monitoring of Leachates in the Vadose Zone

Project ID: 55332

James R. Brainard, Sandia National Laboratories

Research Objective

The objective of this study is to develop and field test a new, integrated Hybrid Hydrologic-Geophysical Inverse Technique (HHGIT) for characterization of the vadose zone at contaminated sites. This new approach to site characterization and monitoring can provide detailed maps of hydrogeologic heterogeneity and the extent of contamination by combining information from 3D electric resistivity tomography (ERT) and/or 2D cross-borehole ground penetrating radar (XBGPR) surveys, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data. Because the electrical conductivity and dielectric constant of the vadose zone (from the ERT and XBGPR measurements, respectively) can be correlated to the fluid saturation and/or contaminant concentration, the hydrologic and geophysical measurements are related.

Research Progress and Implications

As of the 42nd month of a 48-month project, (36 months funding + a 12 month no-cost extension) we have finished developing an inverse procedure for estimating values of unsaturated hydraulic conductivity and moisture release parameters within a three-dimensional (3D) heterogeneous vadose zone model. The procedure can take advantage of pressure head and/or moisture content measurements during transient or steady state flow scenarios to estimate the parameters. It also incorporates statistical information about the geological structure and point measurements of hydraulic conductivity. The model is being tested for its ability to invert parameter values for both deterministic and stochastic cases. Deterministic problems refer to the situations where all values of the head, moisture content distribution, initial and boundary conditions are known, while stochastic problems refer to the cases where the information is either not completely specified or is corrupted. For unidirectional flow in 3D media, the model works well in either case. However the model can encounter convergence problems associated with the nonlinearity in Richard's equation for 3D flow problems. We have implemented a Newton-Raphson iterative scheme to reduce the problem.

We have also investigated the effectiveness of tracer concentration and arrival time information for inverting unsaturated hydraulic parameters. Our results show that the pressure and moisture content data under steady-state flow conditions are more useful for inversion compared to tracer concentration and its arrival time. In addition, new sequential kriging and cokriging techniques have been developed to facilitate future hydrological inversion schemes.

A new stochastic ERT inversion code has been written and tested. Limitations found in the basic stochastic formulation have been alleviated by using an empirical method to increase the a-priori variance in the center of the image region where the sensitivity is small. Also the inversion process is initialized with a starting model that is derived by Kriging apparent resistivity values calculated from ERT measurements made between adjacent electrodes.

A study comparing surveys where data were collected with different electrode configurations has been completed, and it was found that increasing the number of surface electrodes substantially improves image quality. Because surface electrodes are generally less expensive to implement than borehole electrodes, increasing the number of surface electrodes decreases the number of boreholes

needed to monitor a volume, thus reducing implementation costs. These results are being applied to design ERT surveys proposed at a number of DOE sites.

The construction of a test site to test the HHGIT method has been completed. The Sandia-Tech Vadose Zone facility (STVZ) is located adjacent to the New Mexico Tech campus in Socorro, New Mexico, on highly permeable ancestral Rio Grande stratified sand and gravel deposits. Facilities and instrumentation have been designed and constructed to provide a long-term research facility. An infiltration system, located at the center of the instrumented site, has been built to produce a constant flux boundary condition across a 3m by 3m infiltration pad. Thirteen wells cased with PVC provide subsurface access for neutron moisture probes as well as other geophysical devices. Twenty wells have been instrumented with nests of tensiometers, and twenty wells with time domain reflectometry (TDR) probes grouped with tensiometers, suction lysimeters, and thermocouples. Eight vertically installed ERT electrode strings, each with 17 electrodes with .076 meter spacing, and a grid of 36 surface electrodes have also been installed at the site. All instruments have been distributed in an axi-symmetrical pattern about the center of the infiltration pad, and all data collection systems are contained in a building immediately adjacent to the experimental area.

The site has been characterized geologically, hydrologically and geophysically. Geological characterization activities have involved developing a detailed map of subsurface sediments using direct observations in trenches and continuous core samples along with down-hole electrical conductivity logging. Quantitative textural measures have been obtained through particle size distribution analyses performed on one of the continuous core samples at 0.3 m intervals over the entire 11 m of core. Hydrologic characterization consisted of laboratory measurements of samples collected from the continuous core samples during drilling. Measurements have included saturated hydraulic conductivity, pressure versus saturation, and saturation versus electrical resistivity. Geophysical characterization consisted of analyzing pre-infiltration images generated by the ERT and XBGPR methods, as well as other geophysical well logs collected in the PVC access tubes. The different characterization techniques all show approximately 6m of interbedded sand, silt, clay and gravel where moisture contents are highest in the fine grained deposits and lowest in the coarse grained deposits. Underlying the 6 m of interbedded deposits is a more homogeneous fine to medium grained sand with occasional gravel lenses having a correspondingly homogenous moisture content profile.

Infiltration began in early March of 1999 at a rate of 2.7cm/day to produce unsaturated flow conditions. The ERT, XBGPR, neutron and tensiometer data show the wetted bulb expanding primarily downward with time, although some horizontal expansion is present, especially near the clays. The 2D and 3D imaging provided by the XBGPR and ERT, respectively, show the unsaturated flow field to be very heterogeneous in nature. These results emphasize the ability of geophysical imaging to provide more detailed information than that obtained from simple interpolation of down hole or point hydrologic measurements.

Preliminary results showed that standard methods such as Topp's equation for converting XBGPR images of dielectric constant, and Archie's law for converting ERT images of electrical resistivity, do not work well for the materials found at the site. Thus empirical relationships have been derived from lab measurements for conversion of the XBGPR images to moisture content. For the ERT images two different methods have been developed , one based on power-law equations with different coefficients for background and post-infiltration estimates, and the second based on co-Kriging of ERT and neutron data. In addition it appears that the estimates can be improved substantially by incorporating a-priori estimates of the background anisotropy into the ERT inverse models.

Planned Activities

Currently, pressure head and moisture content data sets collected during the field infiltration experiments are being analyzed and pre-processed for use within the hydrologic inversion. Thus in the coming months we will be performing a cooperative inversion in which moisture information estimated from the ERT/XBGPR images will be used as input into the hydrologic inversion scheme to produce better estimates of subsurface hydrologic parameters. In addition, we are using the well

log and continous core data along with the pre-infiltration geophysical images to construct multiple 2D and 3D hydrologic models. The infiltration experiment will then be simulated using these hydrologic models, and the changes in simulated moisture content compared to those observed in the geophysical images.

Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by Accelerator Mass Spectrometry

Project ID: 55148

Dr. Gregory Nimz, Lawrence Livermore National Laboratory

Research Objectives

We propose to identify and quantify the geochemical parameters controlling the migration of key radionuclides (^{36}Cl, ^{90}Sr, ^{93}Zr, ^{99}Tc, and ^{129}I) in undisturbed soils of the shallow and deep vadose zone. Currently, the scientific understanding of these parameters cannot sufficiently meet the requirements for at least two determinations necessary for environmental management in the United States: moisture flux through unsaturated soils, and contaminant radionuclide migration in the far-field environment. The proposed radionuclide measurements will be made using newly developed techniques employing accelerator mass spectrometry (AMS), which provides the required analytical sensitivity such that this work can be conducted for the first time. The research is composed of five components: (1) developing the AMS analytical methods for ^{90}Sr, ^{93}Zr, and ^{99}Tc, and improving AMS methods for ^{36}Cl and ^{129}I; (2) using ^{36}Cl and elemental chlorine analyses from samples collected from a shallow-zone trench and an existing deep-zone (450 meter) drill core to define moisture flux throughout a thick vadose zone in southern Nevada; (3) measuring the distribution of ^{90}Sr, ^{93}Zr, ^{99}Tc, and ^{129}I relative to the defined moisture flux in the shallow vadose zone (where these nuclides occur due to atmospheric nuclear testing); (4) developing a numerical model based on these data that simulates the transport of these radionuclides using a flow-and-transport computer code previously developed at LLNL; and (5) using this numerical model and the moisture flux information obtained from the deep core to simulate the behavior of ^{90}Sr, ^{93}Zr, ^{99}Tc, and ^{129}I in the deep vadose zone. Our investigations in the shallow-zone, where the relationship between nuclide concentration and soil characteristics (composition, texture) can be identified, are expected to greatly improve our understanding of the relationship between chlorine-^{36}Cl distribution and moisture flux. The work on the deep-zone, and the resulting numerical model, is expected to provide a much clearer understanding of the potential for radionuclide transport far away from the contaminant release point, in an environment that is otherwise natural and undisturbed (i.e., in the far-field environment). The radionuclides targeted in this study were distributed globally during the era of atmospheric nuclear testing, and occur in virtually all geological and biological environments. Our development of ultrasensitive AMS techniques for their detection in small samples will provide the means to assess radionuclide migration in most of these environments. This will result in a far greater understanding of potential health risks in the far-field environment, where the public is most likely to come into contact with contaminants. The targeted radionuclides are not only themselves common contaminants, but also are representative of classes of radionuclides and heavy metals that exhibit similar migration behavior. The models developed in this research will therefore furnish a foundation for a wide variety of contaminant migration assessments.

The Development of Aqueous Thermodynamic Models: Application to Waste Tank Processing and Vadose Zone Issues

Project ID: 70163

Dr. Andrew R. Felmy, Pacific Northwest Laboratory

Research Objectives

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

In developing accurate thermodynamic models for these solutions one of the most important factors is identifying the aqueous species present. Identifying these species in tank solutions presents some difficult challenges since, 1) current analytical methods for examining speciation in simple solutions, such as UV-VIS, Raman, etc., develop difficulties in interpreting or analyzing spectral features when multiple complexes are present and contribute to the observed spectra, 2) the solubility of the compounds of many elements, including the actinide elements, is very low under high base conditions. Determining the aqueous speciation in such solutions, which is still needed to predict changes in solubility, is currently done largely by curve-fitting solubility data to hypothesized speciation schemes. Clearly, new and improved approaches to this problem are needed. In order to circumvent these difficulties we have implemented a comprehensive approach which involves coupled experimental solubility studies, spectroscopic measurements of solution speciation, molecular modeling studies which yielded information on species structure and energetics, and thermodynamic modeling efforts using the Pitzer thermodynamic model which is valid to high ionic strengths. In developing this approach we have classified the speciation reactions in tank solutions into three areas: simple inorganic speciation reactions involving the addition of one or more ligands to a metal center, organic chelate binding to a metal center where the chelate completely/incompletely wraps the metal center, and systems where the binding ligand polymerizes forming multiple species which can interact with the metal ion. Examples of each of these types of reaction that effect waste tank and vadose zone applications for the actinides or fission products are described below.

The most important simple inorganic speciation reactions that can occur in these solutions involve the addition of multiple hydroxyl (owing to the high base concentration) or carbonate ligands to the metal center. For example, the addition of one carbonate ligand to the Sr^{2+} cation can result in an asymmetric complex with a strong dipole moment. Under lower base conditions, water molecules bind to the positive part of the dipole (i.e. the Sr ion) to partially neutralize the charge asymmetry. Under higher base or carbonate concentration these water molecules are replaced with either additional carbonate ligands or hydroxyl groups. In the case of Sr, hydroxyl association is very weak and the speciation is dominated by carbonate complexation. In the case of more hydrolyzable metal ions, such structural asymmetries can result in mixed complex formation. However, for larger multi-functional group organic chelates, such as EDTA or HEDTA the chelate cannot completely surround the metal center (Figure 1) which then becomes associated with hydroxyls at high base concentration. This results in the formation of metal-chelate-hydroxyl complexes that can increase the solubility of trivalent actinide compounds by orders of magnitude in basic conditions. An example of this effect is shown in Figure 2 for the solubility of $Eu(OH)_3(c)$, a trivalent actinide analog. The formation of a

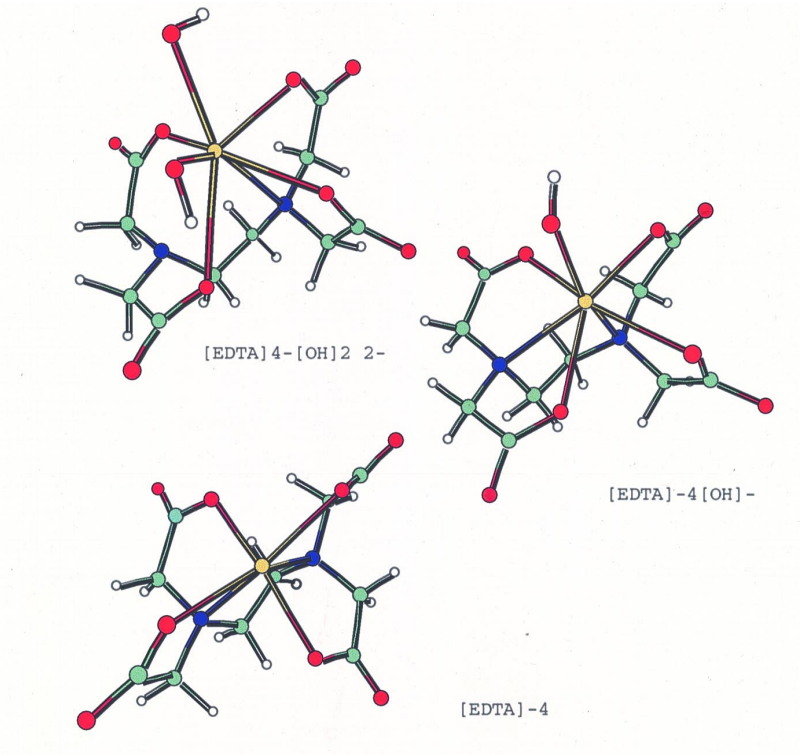


Figure 1. La-EDTA-OH clusters exhibiting the location of OH groups in the complexes.

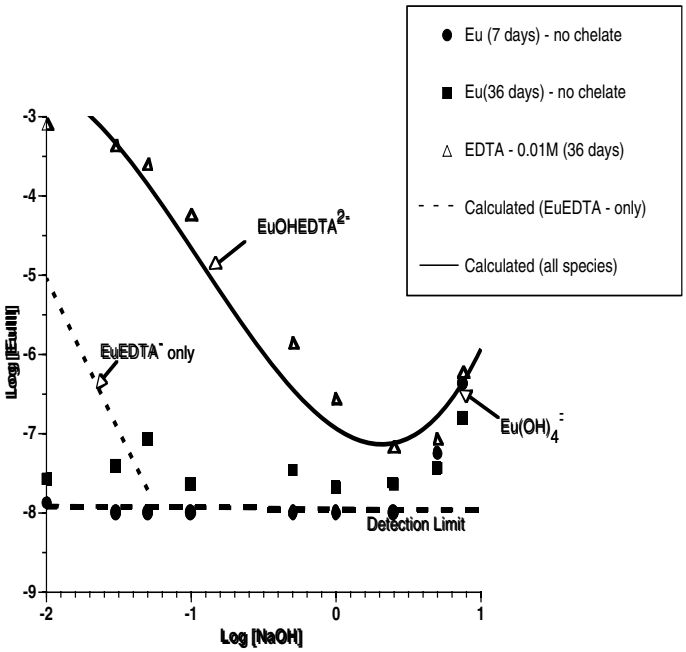


Figure 2. The effects of Eu-EDTA-OH complexation on $Eu(OH)_3$ solubility at high base.

stoichiometric $EuOHEDTA^{2-}$ species increases the solubility by 2 to 3 orders of magnitude over predictions using a simple EuEDTA- species. These increase in solubility and changes in speciation can dramatically effect tank processing strategies, since the desire is to retain the actinides and fission products in the sludges rather than develop costly removal strategies.

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

Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes

Project ID: 54585

Dr. Frank W. Schwartz, The Ohio State University

Dr. Hubao Zhang, Duke Engineering and Services Inc.

Research Objective

When dissolved in groundwater, DNAPLs provide an extremely difficult challenge in removing them from the subsurface. As a potential remediation method, potassium permanganate has been widely used as a powerful oxidant in organic synthesis. The goals of this study are (1) to elucidate the basic mechanisms by which potassium permanganate oxidizes common chlorinated solvents, various constituents in aqueous solution, and porous-medium solids, and (2) to assess the potential for chemical oxidation by potassium permanganate to serve as a remedial scheme involving either source zone flooding or reactive barriers. The study is organized with a laboratory component that looks generally at the basic reaction processes and kinetics, and a theoretical component that is developing modeling tools appropriate for designing systems under field conditions.

Research Progress and Implications

This part summarizes work after 3.5 years of a 4-year project. The work mainly consists of six parts. Part (1) is a fundamental study of kinetic reactions between permanganate and five chlorinated ethylenes including PCE, TCE, and three isomers of DCE. Rate parameters were estimated in the range of pH 4-8. Permanganate consumption by other organic compounds was also estimated for field applications and to predict the TCE degradation rate in a system involving multiple contaminants. Part (2) involves series of kinetic experiments conducted to identify products and to parametize the oxidation kinetics in an attempt to assess the utility of this reaction as the basis for the in-situ remediation of groundwater contaminated by chlorinated ethenes. Based on our understanding of various processes involved with TCE oxidation, a kinetic model was developed and the model parameters were estimated. The kinetic model proposed in this study successfully simulates observed experimental data. Part (3) presents our effort to increase the reaction rate of permanganate oxidation focused on phase-transfer-catalysis. Phase transfer catalysts (PTC) work by transferring permanganate ion into the nonaqueous phase where it initiates oxidation decomposition. Selected PTCs increased the rate of TCE decomposition by catalyzing permanganate oxidation in the organic phase. This study suggests that there is significant potential for testing this scheme under field conditions. Part (4) of the study examined the influences of pentyltriphenylphosphonium as a PTC on the rate of permanganate oxidation of DNAPLs (TCE, PCE, TCA, and PCA) in pure phases and mixtures. TCA and PCA appeared to increase the permanganate consumption significantly when then were mixed with TCE or PCE. The increase in consumption rates with the PTC was most remarkable with the mixtures of PCE and TCA. The PTCs appeared to be promising in their ability to increase oxidation rates of DNAPL mixtures (Figure A). Another aspect of the study investigated efficiency problems related to permanganate oxidation schemes [Part (5)]. Those problems cover competitive permanganate utilization in aquifer materials, manganese dioxide precipitation around zones of high DNAPL, and permeability-related flow bypassing. The results shows a dramatic consumption of permanganate by aquifer materials and mass removal rates are also greatly influenced by the manganese dioxide precipitation and flow bypassing. It is anticipated that in actual field settings, the issue of flushing efficiency needs to be considered in the design (Figure B). A theoretical framework for the chemical

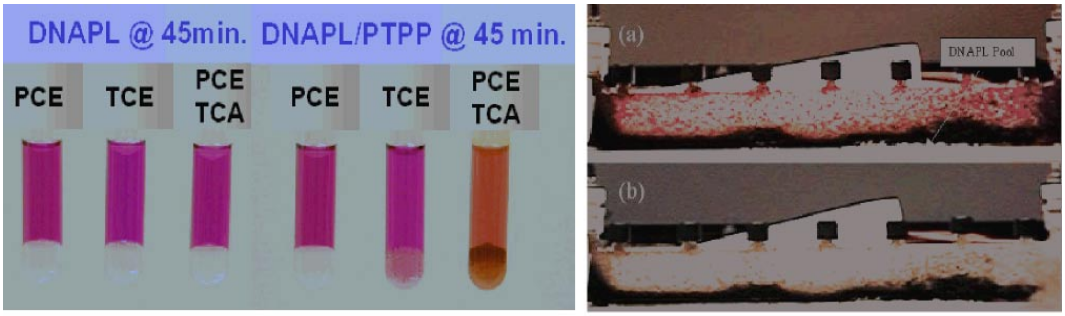
and physical processes was created in part (6). A computer model was developed to simulate the coupled processes of DNAPL dissolution, chemical reaction, and solute mass transport in the in-situ chemical oxidation scheme. The capabilities of this code were tested using already published results of column, test cell, and field experiments. The simulated results matched well with experimental measurements. The computer model provides a useful tool for assisting the design and the prediction of the oxidation processes under field conditions.

Planned Activities

Further research includes detail investigation on mechanisms of permanganate oxidation in nonaqueous phase, cosolvent assisted permanganate oxidation of dissolved DNAPLs, autocatalytic reaction kinetics, and the limitations of permanganate-based remediation scheme.

Information Access

10 papers have been prepared or submitted (see info. following for availability). The results of all these efforts and published references are presented in a 69 page comprehensive report entitled *"Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zones*", which is available at www.geology.ohio-state.edu/~hydro or also from the PI. We are presently preparing disk copies for broad distribution at the upcoming Battelle conference in Monterey and DOE workshop in Atlanta.



(A) (B)

Figure. (A) Test tubes demonstrating the fast reaction in the mixture of PCE and TCA with the presence of PTPP as a PTC, (B) digital images of permanganate flooding of a small glass flow tank. Panel (a) shows conditions after 2 days of flooding. Panel (b) shows conditions 5 hours after flooding stopped. The TCE was sequestered as a rind of precipitate forms and permanganate bypassed this zone.

The Efficacy of Oxidative Coupling for Promoting In-Situ Immobilization of Hydroxylated Aromatics in Contaminated Soil and Sediment Systems

Project ID: 54548

Dr. Walter J. Weber, Jr., University of Michigan

Hildegarde Selig, University of Michigan

Research Objectives

Many hydroxylated aromatic compounds (HACs), particularly small molecules such as substituted phenols, are common contaminants of surface and subsurface systems. The high environmental mobility of these contaminants, due to their relatively high water solubilities, is of particular concern. Abiotic and enzymatic oxidative coupling of this class of contaminants by natural sorbents may be significant in controlling the mobility of HACs and facilitate remediation efforts. The principal objectives of this study are to investigate: 1) the role of abiotic/enzymatic coupling reactions on the sequestration of HACs by natural sorbents; 2) the effects of sorbent structure and chemical composition on such sequestration; and 3) optimal conditions for the induction of these abiotic/enzymatic coupling reactions by addition of suitable catalysts and sorbents. Information gathered from the study will be useful in quantifying the behavior of this class of organic compounds in various subsurface contamination scenarios relevant to DOE facilities, and in specifying strategies for the selection and design of remediation technologies.

Research Progress and Implications

During the third year of this four-year project, significant advances were achieved in the understanding of hydroxylated aromatic compounds (HACs) sequestration by natural sorbents and the induction of oxidative coupling reactions by metal oxide and enzyme additions. As scheduled, the investigation of HAC coupling in natural systems (Phase I of the project) was fully completed this year. The expansion of the experimental matrix to five natural sorbents (Table 1) further confirmed the work of prior years concerning the effect of diagenesis of the carbon fraction (i.e., chemical structure) on the sequestration of HACs by natural sorbents. In this study, sequestration is quantified in terms of the amount of contaminant remaining on the sorbents after sequential water and solvent extractions.

Table 1. Relevant characteristics of the selected natural sorbents used in this study.

Sorbent	[1]S_A, m^2/g	% organic matter	Type of organic matter	[2]Chemistry of organic matter	Mn, ppm	Fe, ppm
Lachine shale	15.0	12.6	kerogen	aliphatic, aromatic	23.2	840
Fox Forest	4.5	5.9	humus	O-aliphatic, phenolic, aromatic	44.8	9
Fox Grassland	8.9	2.5	humus	O-aliphatic, phenolic, aromatic	24.2	16
Wagner III	1.5	0.15	kerogen/humus	n/d	n/d	n/d
Canadian Peat	2.3	99.1	peat	O-aliphatic	13	91

1) S_A = BET surface area determined by N_2 adsorption, 2) predominant groups determined by solid state ^{13}C NMR spectra, n/d = not determined

The results confirm our initial hypothesis that sequestration of HACs in abiotic and non-enzymatic conditions via oxidative coupling is more likely to take place in natural sorbents that have geologically young organic matter (OM) with sufficient reactive groups and mineral catalyst concentrations. Phenolic and oxygen-substituted aliphatic (O-aliphatic) compounds have been reported to participate in oxidative coupling reactions[(1)]. Oxidative coupling reactions are known to be catalyzed by Mn(III/IV) and to a lesser extent by Fe(III) oxides[(2)]. Abiotic and non-enzymatic conditions were maintained by gamma irradiation of the sorbents and additions of the microbial and peroxidase inhibitor sodium azide.

Sorption was non-linear, hysteresis was high, and the sequestration of phenol, o-cresol and p-chlorophenol was significant in the near-surface Fox series soils (Forest and Grassland) (Table 2). These soils contain high concentrations of phenolic and O-aliphatic groups and potentially oxidized forms of Mn/Fe minerals (Table 1). On the contrary, almost total extractability of all three contaminants was observed on Lachine shale and Canadian peat, indicating the absence of oxidative coupling to these sorbents OM (Table 2). The shale, containing diagenetically older kerogen-type OM, may not have sufficient reactive groups for coupling (Table 1). Whereas the peat may not have sufficient oxidized minerals to catalyze the reaction due to the anoxic conditions prevalent in such high organic content soils. In the case of Wagner soil, a sandy material with low organic content composed of mostly kerogen-type OM, similar hysteresis and low sequestration, as seen with shale, were observed (Table 2).

Table 2. Selected parameters that illustrate the sorption linearity (n), sorption-desorption hysteresis ($H.I._{250}$) and extractability (% Seq) of phenol, o-cresol, and p-chlorophenol in natural sorbents described in Table 1.

	phenol			o-cresol			p-chlorophenol		
	[1]n	[2]$H.I._{250}$	[3]%Seq	[1]n	[2]$H.I._{250}$	[3]%Seq	[1]n	[2]$H.I._{250}$	[3]%Seq
Lachine shale	0.80	0.18	4.5 ± 1.1	0.74	0.25	4.6 ± 1.1	0.54	0.31	2.1 ± 0.3
Canadian Peat	n/d	n/d	n/d	0.91	0.05	4.6 ± 1.6	0.85	0.001	1.0± 0.07
Fox Forest	0.76	0.67	74 ± 10	0.87	0.49	19 ± 3	0.61	0.24	61 ± 18
Fox Grassland	0.78	0.51	48 ± 6	n/d	n/d	n/d	0.65	0.49	n/d
Wagner III soil	n/d	n/d	n/d	0.82	0.22	4.7 ± 0.2	0.74	0.29	1.3 ± 0.2

1) n = Freundlich n ($q_e = K_F C_e^n$), 2) $H.I._{250}$ = hysteresis index at C_e = 250 mM. H.I.= $(q_{e,des} - q_{e,ads})/ q_{e,ads}$, 3) % Seq is the percentage of the sorbed fraction (q_e) that remains in the solid after water/solvent extraction averaged for all organic concentrations tested 10 μM ≤ C_o ≤ 1000 mM.

Experiments in soil-free systems with MnO_2 minerals (synthetic birnessite) and horseradish peroxidase (Phase II) have brought important insights about oxidative coupling of HACs. Soil-free experiments with these catalysts confirmed the occurrence of oxidative coupling as shown by the formation of more hydrophobic products detected by HPLC and large polymers that precipitate out of solution after centrifugation. Results obtained to date revealed that the rate of polymer formation and the composition of the polymers could be controlled by varying the catalyst/HAC ratio and contact time. For example, at low birnessite concentrations (0.1 mg/mL), only 22% of the HACs precipitate out of solution compared to 68% for higher MnO_2 concentrations (2 mg/mL) after a contact time of 15 days at equal HAC concentrations. When using horseradish peroxidase (HRP) as the catalyst, polymeric precipitates were observed at phenol concentrations of 1000 and 500 μM but not at concentration of 100 μM or lower. Results obtained to date in engineered systems (Phase III), described in the following paragraphs, suggest that the rate of HAC polymerization may affect HAC sequestration by natural sorbents.

As part of Phase III of this study, synthetic birnessite and HRP were independently added to selected natural sorbents to evaluate the sorption-desorption and extractability of the reaction products under batch equilibrium conditions. Based on differences in the sorption/desorption behavior on

Lachine shale compared to the four other sorbents, it appears that enzyme or mineral additions may enhance coupling to sorbents with peat and humus-type OM but not to those containing kerogen-type OM. Our results show that addition of both catalysts greatly increased the removal of contaminants from solution for all sorbents tested. However, in the case of Lachine shale, contrary to the peat and humus-type OM sorbents, inspection of the sorption/desorption curves indicate that most of the removal was due to precipitation of polymeric material. Freundlich n parameters much greater than 1, and increased hysteresis with increasing organic concentration are suggestive of precipitation. Since batch equilibration followed by centrifugation cannot discriminate between polymeric precipitates and soil-bound fractions, more conclusive results are expected from our flow-through systems.

All the experimental procedures to test HAC sequestration by natural sorbents in flow-through systems were developed during this past year. A packed-bed multiple column system was selected over our original multi-port single column design. Each of the two multiple column systems consists of 1) a multiple syringe pump with capacity for four 25-mL gas-tight glass syringes, 2) four air-tight short glass columns (8 mL bed volume), and 3) a four-column capacity automatic fraction collector. These systems have the ability to test up to eight conditions simultaneously, and the short bed gives the advantage of fast experimental times. Different control situations have been tested (e.g., glass bead packed columns and bromide tracer studies) resulting in negligible losses and low dispersivities in the systems. Initial results showed that 30% of the p-chlorophenol added to the MnO_2-amended system and 25% of the p-chlorophenol added to the soil-only system could not be solvent extracted from Fox Forest soil-packed columns (Figure 1). Since settling of large polymeric materials is not expected in flow-through conditions, the non-extractable fraction is believed to correspond to contaminant incorporated onto the OM by coupling. Parallel investigations in glass bead-packed columns amended or not with MnO_2 showed that large phenolic polymers (i.e., polymers that precipitate after centrifugation) were not formed under the experimental conditions tested. This result independently confirms that coupling to sorbents' OM is the dominant mechanism of removal and suggests that the rate and composition of polymer formation warrants further investigation.

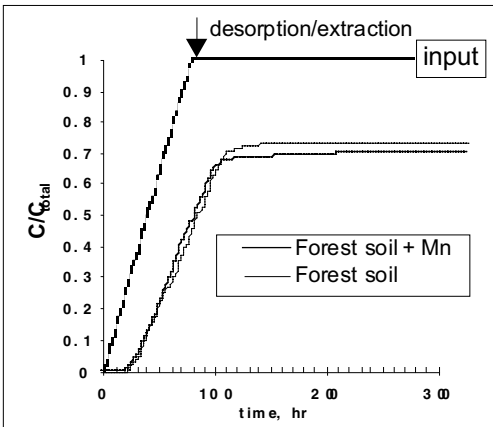


Figure 1. Cumulative mass fraction input/output of 4-chlorophenol in Fox Forest soil-packed flow through columns.

Planned Activities

Experiments are planned to cover two interrelated areas of research: i) sorbent-free model experiments to determine the rate and composition of reactive products at different catalyst and organic concentrations, and ii) sorbent-packed flow-through columns amended with tested catalyst/organic ratios and organic residence time to determine HAC sequestration. Results obtained are expected to be decisive with respect to evaluating HAC coupling as potential component of reactive barrier remediation strategies.

Literature Cited

(1) Stone, A.T. and J.J. Morgan. *Environ. Sci. Technol*. **1984**, 18, 617.
(2) McBride, M.B. *Soil Sci. Soc. Am. J.*, **1987**, 51, 1466.

Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil

Project ID: 55014

Dr. Robert W. Taylor, Alabama A&M University

Research Objective

The effective remediation of DOE superfund sites contaminated by toxic heavy metals has been hampered by the paucity of knowledge about the kinetics and mechanism(s) of heavy metal retention/release by site media particles. Thus remediation strategies have been costly and ineffective.

The information acquired in this project should assist in improving remediation strategies for toxic heavy metals contaminated soils. The objectives are:

1. To determine the effects of residence time on the mechanisms of heavy metals [i.e., Cr(IV), Cu(II), Co(II), and Pb(II)] sorption/release on soil clay mineral surfaces using kinetic studies coupled to extended x-ray absorption fine structure (EXAFS) spectroscopy and fourier transform infrared (FTIR) spectroscopy.
2. To study the effect of temperature, pH, and phosphate on metal sorption by clay minerals and derive thermodynamic parameters to describe the sorption process.

Research Progress and Implications

As of June, 1998 lead sorption in a common soil clay mineral in its pure form (smectite), was investigated by equilibirum sorption studies, coupled with spectroscopic methods. The isotherm and pH edge of lead sorption in the smectite were measured in batch experiments. The sorption isotherms under controlled pH were best-fitted to the Langmuir equation, while those with a fixed pH of 5.5 were best-fitted with the Freundlich equation. The pH-edge of lead sorption shifted to a higher pH as the lead concentration increased. The ionic strength only affected lead sorption in the low pH range. The effects of associated nitrate and perchlorate anions were significant only for lead sorption at high lead concentration (>2 mM). FTIR and XRD spectroscopies were performed with oriented clay samples. In the infrared spectra, a peak with a maximum near 1398 cm^{-1} and a shoulder centered near 1470 cm^{-1} was significant for the samples treated with >1mM lead at pH >5.6. This peak may be composed of several IR bands, including an OH bending band from lead hydroxides and CO_3^{2-} stretching bands from lead carbonates. The basal spacing of lead-treated smectite increased with increasing lead content in the clay and correlated well with the intensity of OH bending band (around 1621 cm^{-1}) of adsorbed water. The increase of basal spacing at low pH (pH <3.3) was poorly correlated with the intensity of water OH bending band.

The effect of pH and phosphate on adsorption of lead and cobalt by the clay mineral kaolin was also studied. Batch equilibrium studies for kaolin and phosphate treated kaolin in contact with metal solutions at pH ranging from 3 to 8 were performed. The sorption of metals from $Pb(NO_3)_2$ and $Co(NO_3)_2$ solutions by kaolin was found to be pH dependent. For both metals, little sorption occurred below pH 6.0; increased sorption was observed around pH 6-7 with maximum sorption at pH 8. However, lead and cobalt control solutions (without clay) indicate that above pH 7, some of the lead and cobalt ions were removed from solution by precipitation.

The pH of maximum sorption was chosen and kinetic studies performed for periods ranging from 5 minutes to 3 months. The results indicated that reaction equilibrium was attained within 10 minutes. Furthermore investigations on effect of lead sorption on phosphate treated (phosphate adsorbed on clay first then lead adsorbed to clay surface) revealed that lead sorption significantly increased with phosphate already present on the surface (compared to phosphate free surface); with maximum sorption

in pH 6-8 range. Kinetics of lead sorption on kaolin-phosphate surfaces indicated a very fast reaction which reached equilibrium within 10 minutes over a 3 month study period (i.e., there was no change in the quantity of lead sorbed after 10 minutes). On the other hand, cobalt sorption decreased on the kaolin-phosphate surface compared to the phosphate free kaolin surface. In our future studies these results will be further investigated. We conclude that these reactions require fast kinetics methodology (i.e., pressure jump technique) to elucidate their mechanisms.

The lead and cobalt sorption phenomena is further being investigated using EXAFS spectroscopy. EXAFS spectra for lead and cobalt sorbed to phosphate free kaolin as well as kaolin-phosphate surfaces were recently collected from Brookhaven's National Synchrotron Light Source. The next step is to resolve the spectra in an attempt to discern the type of sorption (i.e., surface complexes) formed between lead and the kaolin surfaces investigated.

Using Cr K-edge x-ray absorption fine-structure (XAFS) spectra, we investigated Cr sorption on oxide surfaces, we found no evidence for Al or Fe atoms in the second atomic shell surrounding Cr adsorbed to oxide minerals. The absence of Al or Fe in the second atomic shell demonstrates that chromate adsorbs by a weak outer-sphere mechanism.

We also examined the reductive capacity of thiol (-SH) groups in soil humic substances. We used S K-edge x-ray absorption near structure (XANES) spectra to quantify the various oxidation states of sulfur in soil humic substances, including thiol sulfur.). The reaction between Cr(VI) and humic substances, followed using both Cr K-edge and S K-edge XANES, revealed humic substances reduce Cr(VI) to Cr(III) using thiol instead of quinone groups, the reducing agent most soil chemists believe to be important in redox reactions.

We also studied sorption of Cu(II) by oxide and hydroxy-interlayer layer silicates. The tendency of Cu(II) ions to form surface precipitates depends on the oxide surface they are adsorbed to. Using both x-ray absorption spectroscopy and electron paramagnetic resonance, we found that Cu(II) forms hydroxide precipitates on silica surfaces at loadings as low at 5% of a monolayer while no Cu(II) precipitates form on alumina surfaces at 20% monolayer coverages. We also found that Cu(II) binds to the interlayer hydroxide in adsorption experiments using hydroxy-interlayer clay minerals. Hydroxy-interlayer clay minerals are common in the B-horizon of Altisol and Ultisols found in humid climate along the East Coast of the U.S.

Planned Activities

We will request a 6 months no cost extension of the project. During that time we intend to further investigate the sorption of lead and cobalt on kaolin surface with and without phosphate already sorbed. EXAFS and FTIR spectroscopies will be used to acquire surface chemical information. Also equilibrium isothermic experiments will be performed at different temperature, pH and ionic strengths to acquire thermodynamic data and further elucidate the sorption phenomena between lead and cobalt on kaolin surface with and without phosphate already sorbed.

Other Access to Information

Presentations

Shen, S., Taylor, R. W., Bleam, W. F., Tu, S. I., 1998. Coupled reduction-sorption of chromate in dithionite-reduced smectites, Agronomy Abstracts, Baltimore, MD, p. 189.

Bleam, W. F., Helmke, P. A., Szulczewski, M. D., Bloom, P. R., Taylor, R. W., Weesner, F. J., Xia, K., 1998, Recent advances in understanding the chemistry of Cr(VI), Pb(II) and Hg(II) in soils, Agronomy Abstracts, Baltimore, MD, p. 36.

Szulczewski, M. D., Xia, K., Helmke, P. A., Bleam, W. F., Taylor, R. W., 1998, Evaluating the reductive capacity of humic substances: Reactions between thiol/thio groups and chromate, Agronomy Abstracts, Baltimore, MD, p. 38.

Taylor, R. W., Shen, S., Bleam, W. F., Tu, S. 1999. Chromate removal by dithionite-reduced clays. 5th International Conference on the Biogeochemistry of Trace Elements, Vienna Austria, July 11-15, 1999.

Referred Publications

Shen, S., Taylor, R. W., Bart, H., Tu, S. 1999. Equilibrium and spectroscopic studies of lead retention in smectite. Commun. Soil Sci. Plant Analysis (in press).

Calcite Precipitation and Trace Metal Partitioning in Groundwater and the Vadose Zone: Remediation of Strontium-90 and Other Divalent Metals and Radionuclides in Arid Western Environments

Project ID: 70206

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Research Objectives

Radionuclide and metal contaminants are present in the vadose zone and groundwater throughout the U.S. Department of Energy (DOE) weapons complex. Demonstrating in situ immobilization of these contaminants in vadose zones or groundwater plumes is a cost-effective remediation strategy. However, the implementation of in situ remediation requires definition of the mechanism that controls sequestration of the contaminants. One such mechanism for metals and radionuclides is co-precipitation of these elements in authigenic calcite and calcite overgrowths. Calcite, a common mineral in many aquifers and vadose zones in the arid western U.S., can incorporate divalent metals such as strontium, cadmium, lead, and cobalt into its crystal structures by the formation of solid solutions. The rate at which trace metals are incorporated into calcite is a function of calcite precipitation kinetics, adsorption interactions between the calcite surface and the trace metal in solution, solid solution properties of the trace metal in calcite, and also the surfaces upon which the calcite is precipitating. A fundamental understanding of the coupling of calcite precipitation and trace metal partitioning and how this may occur in aquifers and vadose environments is lacking.

The focus of the research proposed here is to investigate the facilitated partitioning of metal and radionuclides by their co-precipitation with calcium carbonate. Our specific research objectives include

- Elucidating the mechanisms and rates of microbially facilitated calcite precipitation and divalent cation adsorption/co-precipitation occurring in a natural aquifer and vadose zone perched water body as a result of the introduction of urea.
- Assessing the effects of spatial variability in aquifer host rock and the associated hydro/biogeochemical processes on calcite precipitation rates and mineral phases within an aquifer and a vadose zone perched water body.

Research Progress and Implications

This report summarizes project activities after 5 months of a 36-month project. Water samples were collected from wells in the Eastern Snake River Plain Aquifer (SRPA); three were located on the INEEL and one just south of the site boundary. All groundwater samples tested positive for urease activity, in both liquid and solid media. Other groundwater samples collected from elsewhere in eastern Idaho also universally tested positively, indicating that urease activity is indeed common in the SRPA. Twelve ureolytic SRPA isolates were obtained from the urea agar plates. Fatty acid methyl ester (FAME) profiles were obtained for all twelve isolates. Principal component analysis of

FAME results indicated that the isolates could be divided into three main groups. Based on these results, one member of each group was selected for further characterization. All three of the isolates were gram negative rod-shaped heterotrophs, but the carbon source utilization potential results indicated differences between the isolates. However, for all three organisms amino acids appeared to be oxidized most rapidly. Limited phylogenetic analysis performed on the isolates indicated that all three likely had 16S rRNA gene sequences very similar to previously described isolates or clones. Because the partial gene sequences obtained for the SRPA isolates were so similar to previously reported sequences, the acquisition of sequence data for the entire 16S rRNA gene was not pursued further.

The ability of SRPA isolates to hydrolyze urea and precipitate calcite was demonstrated in batch experiments. Cells used in the calcite precipitation experiments were already induced for urease expression, and upon initiation of the experiments the hydrolysis of urea was confirmed by the immediate increase in pH and the production of ammonium. By the end of the eight-hour experiment, the pH in all of the cultures reached similar values, around pH 8.3-8.5. Experimental result suggests that the urease activity in the SRPA isolates is significantly lower than in the *Bacillus pasteurii* reference culture. In all cases however the ammonium concentrations increased linearly with time in the experimental cultures.

In all of the cultures, visible white precipitates developed within the first half-hour after inoculation. This was consistent with geochemical modeling using MINEQL, which predicted that while the medium was initially almost two orders of magnitude under-saturated with respect to calcite, the introduction of less than 1 mM $(NH_4)_2CO_3$ would cause calcite supersaturation. Based on the measured ammonium production rates, this supersaturation likely occurred within the first 12 to 24 minutes of culture growth. The identity of the precipitates as calcite was confirmed by X-ray diffraction. Scanning electron microscopy revealed both spherical and amorphous morphologies, with microbes in close association with the minerals.

Dissolved calcium measurements also confirmed the transfer of calcium into the solid phase. The production of ammonium was correlated with the precipitation of calcite. Comparison of MINEQL predictions for the expected drop in dissolved calcium concentration as a function of ammonium concentration with actual measured values from the experiments imply that dissolved calcium concentrations were controlled effectively by the equilibrium solubility of calcite. The results indicate that the generation of two moles of ammonium (or the hydrolysis of one mole of urea) results in the removal of one mole of calcium from solution. This corresponds to the reaction:

$$H_2NCONH_2 + 2H_2O + Ca^{2+} \rightarrow 2NH_4^+ + CaCO_3$$

In this system then, the rate of calcite precipitation is directly linked to the rate of urea hydrolysis. For field application of the proposed remediation technology, the demonstration of a direct link between the urea hydrolysis and calcite precipitation reactions will be important, because it will not be possible to recover and accurately quantify calcite precipitates from the subsurface. Rather, it will be necessary to confirm and monitor urea hydrolysis and pH, as indirect evidence that carbonate mineral precipitation is occurring in the aquifer as a result of the introduction of urea.

The results of our preliminary evaluation of the potential for utilizing urea hydrolysis as the basis for an in situ remediation technique for ^{90}Sr and other divalent contaminants in SRPA groundwater are promising. Urea hydrolyzing organisms are common in the aquifer, and they can catalyze precipitation of calcite similarly to the known urease positive organism *B. pasteurii*.

Planned Activities

During the remainder of the first year of this project experiments under conditions more closely simulating natural SRPA groundwater will be conducted to determine whether the observations derived in this study are applicable to environmental conditions. In addition, experiments including trace levels of strontium and or uranium are planned. Preliminary results suggest that the incorporation of trace metals significantly influences the morphology of the precipitated calcium carbonate and in the case of strontium can result in the formation of aragonite rather than calcite. During the second year an in situ experiment is planned in a single groundwater well at the INEEL.

Information Access

R.D. Lawson, Y. Fujita, F.G. Ferris, F.S. Colwell, and R.W. Smith, "Microbially Accelerated Calcium Carbonate Precipitation for Radionuclide Sequestration: Preliminary Laboratory Evaluations of Urea-Hydrolyzing Organisms (abs.)," Amer. Geophys. Union Fall Meeting 1999 *EOS* **80**:H31B-06 (1999).

Experimental Determination of Contaminant Metal Mobility as a Function of Temperature, Time, and Solution Chemistry

Project ID: 55249

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Research Progress and Implications

During the FY96-FY99 funding cycle we examined the uptake of aqueous strontium onto goethite, kaolinite, and amorphous silica surfaces as a function of pH, total strontium, and temperature. Our overall goal was to produce a mechanistic sorption model that can be used in reaction-transport calculations to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment. Our approach was to combine structural information derived from EXAFS analysis together with macroscopic uptake data and surface complexation models to clarify the physical and chemical structure of sorbed complexes. We chose to study these solids because of the prevalence of clays and iron hydroxides in natural systems, and because silica colloids probably form beneath leaking tanks at Hanford as caustic waste is neutralized. We have published the spectroscopic work in two papers in the *Journal of Colloid and Interface Science* [1, 2], and will soon submit at third manuscript *to Geochemical Transactions* [3] combining the sorption and spectroscopic data with a mechanistic complexation model.

Early in the study we learned that strontium sorption was independent of temperature (25 to 80ºC). All subsequent work was conducted at room temperature. Below, we focus this summary on three important conclusions from our study.

(i) Strontium sorbs primarily as a hydrated outer-sphere complexes that are stable for several months over the precipitation of pure strontianite, $SrCO_3(s)$

We collected EXAFS spectra on more than 20 amorphous silica, kaolinite, and goethite samples from pH 4 to 10. With the exception of two goethite samples (see below), the EXAFS analyses suggested that the largest fraction of sorbed strontium on these phases was present as hydrated (i.e., water-ligated) complexes. This interpretation is based on the absence of backscattering atoms beyond the first oxygen shell in the EXAFS spectra. There was no evidence for dehydration of a significant fraction (>50%) of strontium and formation of inner-sphere complexes. We conclusively demonstrated that second-neighbor backscattering would be readily apparent in low-temperature spectra if dehydration occurred based on the analysis of strontium reference compounds [1]. For strontium sorbed to amorphous silica and kaolinite, there was also no evidence in the spectra for backscattering from a carbonate ligand in the presence of dissolved CO_2. The macroscopic sorption data and equilibrium aqueous speciation are consistent with the EXAFS results. Similar sorption behavior in the presence and absence of dissolved CO_2.

(ii) Nucleation of incipient $SrCO_3(s)$ to goethite is tied to carbonate sorption

Limited spectroscopic evidence suggests that the goethite surface may nucleate strontium carbonate precipitation from fairly concentrated solutions ($Sr_{initial} = 10^{-3}$ molal). Results to date indicate that nucleation of a precipitate is related to solution pH and to the sorption of carbonate to the goethite surface (which is dependent on pH), rather than on the saturation state of the solution, and to reaction time. Spectra of samples reacted for short times suggested that $SrCO_3(s)$ nucleation required a critical concentration of carbonate sorbed to the goethite surface, even though reacting solutions for all

samples were supersaturated with respect to $SrCO_3$(s). However, kinetic experiments suggested that the strontium carbonate surface precipitate may be a transitory phase. We observed $SrCO_3$(s) surface precipitates after four days of reaction, when strontium uptake to goethite was greatest. In a sample aged for 57 days, we observed only outer-sphere complexes and more strontium uptake than for samples aged for shorter times.

(iii) Surface Complexation Model

Our spectroscopic results allow us to constrain the molecular reactions used in the surface complexation models. For amorphous silica and kaolinite, mechanistic models must describe strontium sorption as outer-sphere complexes that retain their primary hydration sheath. Strontium sorption to goethite is more complicated and may require strontium- carbonate surface precipitates or complexes in addition to outer-sphere complexes.

We successfully modeled the uptake of strontium to amorphous silica as an outer-sphere complex over a range of initial strontium concentrations ($[Sr]_{initial} = 7x10^{-6}$ to 10^{-3} molal) and pH (6 to 10) at constant ionic strength. We used deprotonation and surface capacitance constants ($\log K_{>SiO^-} = -2.5$ and $C_1 = C_2 = 6\ Fm^{-2}$) determined by the direct observation of the pH-dependence of >SiOH and $>SiO^-Na^+$ amorphous silica surface sites using nuclear magnetic resonance spectroscopy [4]. From these values and our experimental uptake data, we have determined outer-sphere sorption constants for strontium, $\log K_{>SiO^-Sr^{2+}} = -9.5$, and for sodium, $\log K_{>SiO^-Na^+} = -6.6$.

We modeled the uptake of strontium to negatively charged sites on the kaolinite basal plane as an outer-sphere complex ($\log K_{>PO^-Sr^{2+}} = 0.0$) over a range of initial strontium concentrations ($[Sr]_{initial} = 10^{-5}$ to 10^{-3} molal) and pH (5 to 10) at constant ionic strength. The negative sites on the kaolinite basal plane are due to the isomorphic substitution of Al^{3+} for Si^{4+} in the silica layer. In our model we assumed that the protonation of this site is dependent on pH.

Our efforts to model strontium sorption to goethite as a combination of strontium-carbonate surface precipitates or complexes in addition to outer-sphere complexes was unsuccessful. We suspect that the protonation and deprotonation constants are poorly constrained for goethite because we observed similar strontium uptake to goethite and amorphous silica as a function of pH, even though each mineral has distinct surface properties. General knowledge of mineral surface charge has been derived from the differences in measured and calculated solution pH from acid-base titration. These experiments are problematic because the measured pH is not a unique measurement of the uptake or release of protons; carbonate speciation, mineral dissolution, and electrolyte sorption all effect solution pH. Sorption constants of fundamental protonation-deprotonation reactions must be well constrained before both carbonate and strontium uptake can be modeled accurately within evidence imposed by spectroscopic observation.

Planned Activities

Our renewal proposal picks up where this proposal ended and addresses the ionic strength effects strontium sorption, novel measurement of goethite protonation and deprotonation reactions, solubility and stability of $SrCO_3$(s) precipitates identified on goethite surfaces, and application of mechanistic sorption models to column reaction-transport experiments using Hanford sediments.

References

1. O'Day, P.A., Newville M., Neuhoff, P. S., Sahai, N., Carroll, S. A (2000) *X-ray absorption spectroscopy of strontium (II) coordination. I. Static and thermal disorder in crystalline, hydrated, and precipitated solids and in aqueous solution.* J. Colloid and Interface Science, in press.
2. Sahai, N., Carroll, S. A., Roberts, S., O'Day, P. A (2000) *X-ray absorption spectroscopy of strontium (II) coordination. II. Sorption and precipitation at kaolinite, silica gel, and goethite surfaces.* J. Colloid Interface Science, in press.
3. Carroll, S.A., Roberts, S., O'Day, P. A. (2000) *Strontium Chemistry at Amorphous Silica, Kaolinite, and Goethite Surfaces.* Geochemical Transactions, in prep.
4. Maxwell, R.S., Carroll, S. A., Bourcier, W., Martin, S., Hulsey, S. (2000) *Evaluation of silica-water chemistry using NMR.* Geochimica Cosmochimica Acta, in review.

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

Project ID: 70121

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Research Objectives

Fundamental research is proposed to investigate the role of calcium carbonate grain coatings on the vadose zone chemical reactivity of key Hanford contaminants (i.e., $^{60}Co^{2+}$, $^{90}Sr^{2+}$, CrO_4^{2-}, and $^{99}TcO_4^{-}$). Calcium carbonate is widely distributed through the Hanford vadose zone as a result of current and past geochemical processes, and exists as grain coatings and intergrain fill. It also results from the interaction of high level waste (e.g., high in Na^+ and OH^-) with Ca-saturated subsurface sediments. While secondary iron-, aluminum-, and manganese-oxyhydroxide grain coatings are known to control the sorption chemistry of non-calcareous sediments for inorganic ions, no comparable understanding exists for carbonate grain coatings, which may be equally or more abundant in certain situations. We hypothesize that carbonate coatings enhance the sorption of carbonate compatible contaminants (e.g., ^{90}Sr, ^{60}Co) through a combination of adsorption and co-precipitation processes, but interfere with the reductive immobilization of the oxoanions CrO_4 and TcO^{4-} by passivating electron dense surfaces of Fe^{2+}- minerals such as magnetite and biotite in Hanford sediments.

This project will explore the behavior of calcium carbonate grain coatings including how they form and dissolve (e.g., natural and waste fluid induced), their reactivity toward contaminants under water-saturated and unsaturated conditions, their impact on the reactivity of the mineral substrate, and their in-ground composition and minor element enrichment. The goal is to provide an improved understanding of contaminant sequestration/immobilization reactions that can be scaled to macroscopic reactive transport models used to forecast contaminant migration. Our scientific focus will be on the influence of the coatings on, 1.) surface coordination or co-precipitation reactions, and 2.) electron transfer reactions that can result in the immobilization of redox-sensitive contaminants. Modern surface- and bulk-sensitive structural and imaging methods including X-ray absorption spectroscopy, scanning probe microscopy, photoelectron spectroscopies, and others will be applied in concert with judiciously designed model systems such as epitaxially grown surfaces of known crystallographic orientation and structure to provide a rigorous molecular and microscopic understanding of the controlling reactions of target contaminant ions with carbonate-coated mineral surfaces. Model system studies will be linked with parallel spectroscopic, microscopic, and macroscopic investigations of calcareous Hanford sediments, to provide basic scientific information for the remediation/closure of Hanford and other DOE sites.

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

Project ID: 60355

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Dr. Paul M. Bertsch, Savannah River Ecology Laboratory
R. Jeffrey Serne, Pacific Northwest National Laboratory
Dr. James P. McKinley, Pacific Northwest National Laboratory

Research Objective

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

The research will integrate studies of ion-exchange thermodynamics on the FES, with high resolution surface microscopies and spectroscopy to probe the structure of FES in Hanford sediments and to describe how the chemical environment of sorbed Cs changes when HLW supernatants promote silica dissolution and aluminum precipitation. Newly available atomic-force microscopies and high-resolution electron-beam microscopies afford previously unavailable opportunities to visualize and characterize FES. Our overall goal is to provide knowledge that will improve transport calculations of Cs in the tank-farm environment. Specifically, the research will:

- Identify how the macroscopic sorption behavior of Cs on the micaceous fraction of the Hanford sediments changes after contact with simulants of HLW tank supernatants over a range of relevant chemical ([OH], [Na], [Al], [K, NH_4]) and temperature conditions (23°-80°C).
- Reconcile observed changes in sorption chemistry with microscopic and molecular changes in adsorption-site distribution, chemistry, mineralogy, and morphology/structure of the micaceous sorbent fraction.
- Integrate mass-action-solution-exchange measurements with changes in the structure/site distribution of the micaceous-sorbent fraction to yield a multi-component/site-exchange model relevant to high ionic strength and hydroxide concentrations for prediction of environmental Cs sorption.

Problem Statement

Environmental Management Concerns

- Single Shell Tanks (SST's) containing high level wastes have leaked supernate containing large amounts of radioactive ^{137}Cs (10^6 Ci) and other co-contaminants into the Hanford vadose zone.
- In select locations ^{137}Cs has exhibited "expedited" migration (up to 50 meters when predicted migration distances are < 10 m) saturated zone. The reasons for "expedited" migration are unclear.

- Deep ^{137}Cs migration has been observed beneath the SX tank farm at Hanford with REDOX wastes as the carrier, causing significant regulatory and stakeholder concern.

Scientific Context

- Micaceous 2:1 layer silicates are the primary environmental sorbents of Cs. Cs^+ is strongly sorbed by specific structural sites on these solids that exhibit nanometer scale dimensions with unique steric and geometric attributes.
- Micaceous 2:1 layer silicates exist as a small mass fraction of Hanford vadose zone sediments. These are known to impart significant Cs^+ sorptivity to Hanford subsurface sediments.

Science Issues

- REDOX wastes were self-concentrating by boiling, and contain molar plus concentrations of Na^+, NO_3^-, OH^-, and $Al(OH)_4^-$. The sorption behavior of Cs^+ from this complex waste matrix is not known.
- The chemical composition and temperature of the REDOX wastes is "harsh" and will induce dissolution and precipitation reactions upon contact with Hanford vadose zone sediments, possibly changing mineral surface structure and the selectivity of the micaceous fraction for Cs^+. The extent, kinetics, and impacts of these reactions on contaminant fixation and migration are unknown.
- There exists no literature information upon which to base scientifically credible estimates of Cs^+ adsorptive-retardation beneath SST's that have leaked high pH-high ionic strength waste waters.

Research Progress and Implications

Research since the last time of reporting (May, 1998) has continued to investigate, 1.) the Cs retention characteristics of a mica containing composite sediment from the Hanford formation, and 2.) the mineral association of ^{137}Cs in 35-year old contaminated sediment from beneath a leaked single-shell tank at Hanford (SX-109). Highlights from this work will be presented in the text that follows. Studies to determine the influence of high base on highly selective sorption/exchange of Cs to the micaceous fraction of the Hanford sediments were initiated at the beginning of the fiscal year as planned in the proposal. The results of these experiments are preliminary and are not reported here.

1.) Thermodynamics of Cs Exchange. Adsorption isotherms of Cs were measured over a wide sorbate range on homo-ionic Hanford sediments (Na^+, K^+, Ca^{2+}) in salt solutions of different concentration. The objective of these measurements was to relationships to predict the magnitude of Cs^+ adsorption to Hanford sediment. Salt concentrations ranged between 10^{-2} – 10^{-69} mole/L to bracket those observed in natural and HLW impacted environments. The results were analyzed in terms of a conditional thermodynamic equilibrium constant (K_v) for the generalized exchange reaction:

$$uCs^+_{(aq)} + vAX_u = uCsX + vA^{u+}_{(aq)} \qquad (K_v)$$

where $K_v = [A^{u+}]^v[N_{CsX}]^u/[Cs^+]^u[N_{AXu}]^v$ and N is mole fraction of the exchanger phase components (AX_u, CsX). The mole fractions are defined as follows:

$$N_{CsX} = [CsX]/([CsX] + [AX_u]) \text{ and } N_{Axu} = [AX_u]/ ([CsX] + [AX_u])$$

The K_v is often termed a selectivity coefficient that is a measure of the binding affinity of the sorbate (Cs) relative to the index or saturating cation (e.g., $A^{u+}_{(aq)}$) that was either Na^+, K^+, or Ca^{2+} in this case.

The Cs^+ - Na^+, Cs^+ - K^+, and Cs^+ - Ca^{2+} exchange data each conformed to a single K_v relationship in the different salt solutions {Figure 1., where E(CsX)is the equivalent fraction of Cs on the exchanger [= adsorbed Cs concentration/cation exchange capacity]}. Cs^+ was sorbed in great preference to the other cations, with K_v ranging from 10 to 10^{10}. Consistent with ionic radius and hydration enthalpy, K^+ was the most effective competitor for Cs. The dependence of K_v on E(CsX) indicates the presence of approximately three different types of exchange sites in the sediment with different adsorption/

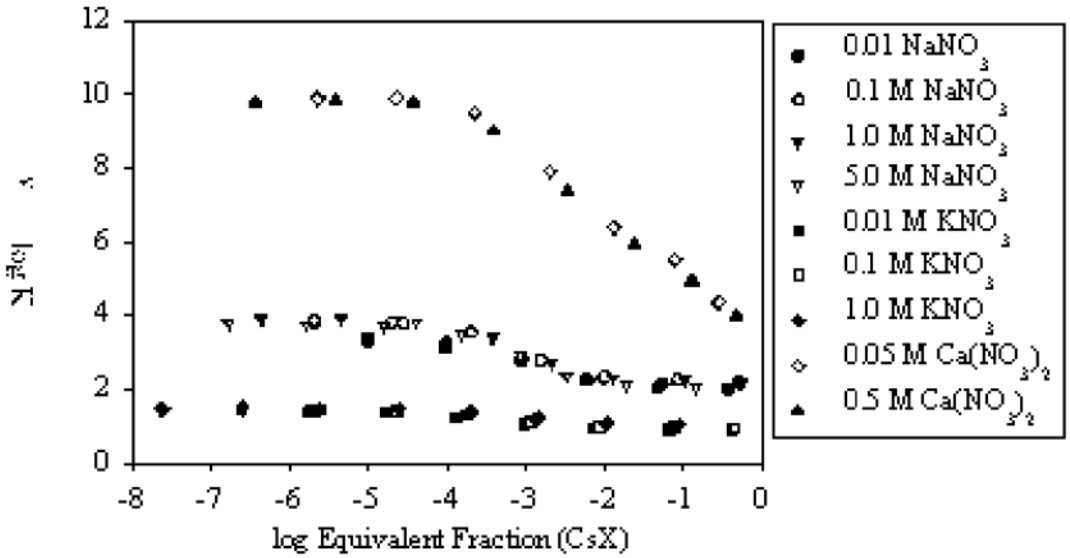

Figure 1. Dependence of the conditional thermodynamic equilibrium constant on surface saturation (CsX) and electrolyte concentration.

exchange energies. A high affinity site is present at low concentration, e.g., log E = 10^{-4}. The high affinity site exists in the sediment at a total concentration of 10^{-8} mol/g, which is 1% of the operational frayed edge site pool defined by silver-thiourea exchange (data not shown). The high affinity site is slightly lower in concentration than is $^{137}Cs^{+}$ in HLW (e.g., 10^{-7} mol/g). The exchange coefficient functions in Figure 1 can be used to model Cs^{+} adsorption by ion exchange in Hanford sediments.

2.) Desorption and Fixation of Cs. Cesium is known to diffuse within the interlamellar space in specimen illites, leading to its partial or complete fixation. Fixation is highly significant in the Hanford sediments. If fixation occurs, ^{137}Cs may be held in place by the geomedia for sufficient periods to allow full decay to daughter products. Fixation, therefore represents a natural attenuation process that may prevent Cs migration to groundwater and that should be quantified as a basis for the "leave-it-in-place" remediation scenario.

Several experiments have been performed to evaluate Cs^{+} fixation and one is shown here. In that experiment, $^{137}Cs^{+}$ (at 10^{-4} mol/L representative of HLW supernatant) was adsorbed to Hanford sediment in two different salt solutions (0.005 and 5 mol/L) and these were allowed to age for periods ranging from 0.5 to 120 day. After the aging period, the salt solutions with residual unadsorbed Cs^{+} were removed and replaced with K^{+} containing electrolyte. The K^{+} was present at a concentration (10^{-2} mol/L) that was 100 times the total Cs^{+} concentration. Cesium concentrations in the aqueous phase were then followed for extensive time periods to assess the extent to which K^{+} induced Cs^{+} desorption from the sediment (Figure 2a,b). Cesium that is not desorbable by 100 times molar excess of K^{+} is effectively fixed. The Y-axis in Figure 2 defines the normalized concentration, C/C_0, where C is the concentration at any time (t), and C_0 is the initial soil bound concentration after the adsorption/aging period. Importantly, the initial adsorbed concentration in 5 mol/L salt (3.7 x 10^{-7} mol/g) was 38 times lower than that in 0.005 mol/L salt (1.4 x 10^{-5} mol/L) as a result of the mass action effect of Na^{+}.

The desorption behavior of Cs^{+} was similar in the two different salt solutions. That is, a significant fraction of the adsorbed Cs was immediately released upon K^{+} addition. After this initial desorption episode that was presumed to be an ion-exchange displacement, little additional Cs^{+} was released by the sediment. There was slight tendency for the shorter-aged samples to release more Cs^{+}, but a distinct correlation with aging time was not observed. In spite of the noted similarity, there was, a major difference in the fractional extent of Cs^{+} desorption in the two salt solutions (Figure 2a,b). In 5 mol/L Na^{+}, approximately 55 % of the adsorbed Cs^{+} was desorbable, while 85 %, on average, was released in 0.005 mol/L Na. However, because significantly more Cs^{+} was adsorbed in 0.005 mol/L

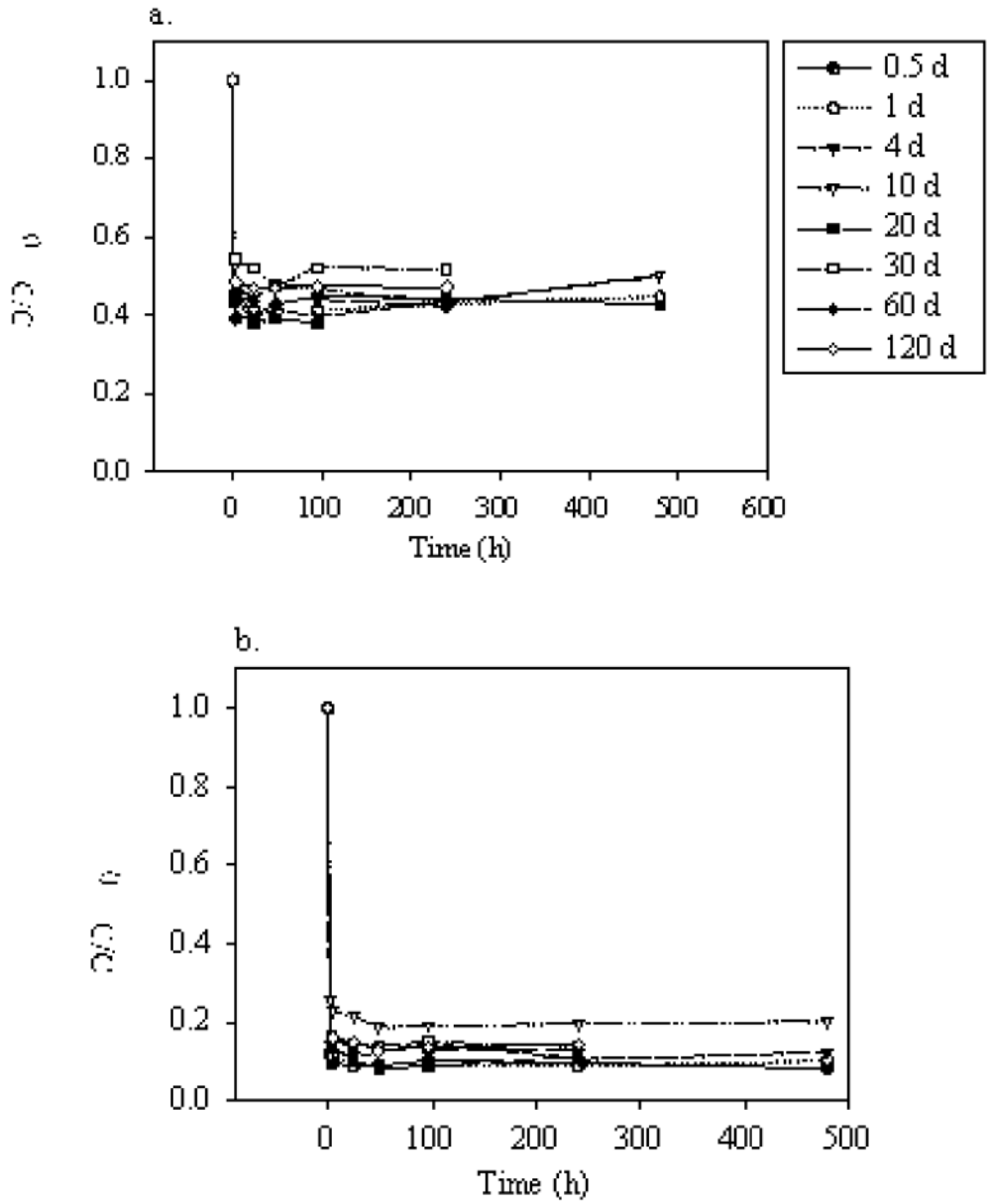

Figure 2. Desorption of Cs^+ from Hanford sediment by 10^{-2} mol/L K^+ after aging from 0.5 to 120 d. a.) Cs^+ contact and aging in 5.0 mol/L NaCl; and b.) Cs^+ contact and aging in 0.005 mol/L NaCl. Initial Cs^+ contact solution was 10^{-4} mol/L Cs^+. C/C_0 is the normalized adsorbed concentration, e.g., the adsorbed concentration at time t (c) divided by the intial adsorbed concentration at the start of desorption.

Na^+, a larger Cs^+ concentration was actually fixed at low salt than at high salt, e.g., 2.10 x 10^{-6} mol/g as compared to 1.66 x 10^{-7} mol/g. These results support two important conclusions: 1.) Cs^+ fixation occurs on only a subset of the high affinity exchange sites and 2.) Na^+ competes with Cs^+ for access to fixation sites. This latter conclusion was unexpected given the significant differences in ionic radius and hydration energy of Na^+ and Cs^+. The fixation process is presumed to involve highly selective exchange followed by the dehydration and interlamellar migration of the Cs^+ ion.

3.) Cs Distribution in Hanford Micas. The differential abilities of micaceous minerals in Hanford sediments to immobilize Cs, and the variable binding of Cs to disparate reactive sites on mica plates, are under investigation using wet-chemical experimentation and compositional imaging. Flakes of

three micaceous minerals (biotite, muscovite, and vermiculite) were identified in Hanford sediments using a binocular microscope and carefully hand-picked and segregated for experimentation. Each mica separate was reacted with Cs, by suspension in solution concentrations of 10^{-2} to 10^{-4} M Cs, for periods of one and three months. The reacted micas were washed and air dried, then mounted as whole flakes or sectioned to expose external and internal surfaces. Micas were hypothesized to preferentially sorb Cs at relatively high energy frayed-edge sites, and to strongly bind Cs by displacement of K at internal sites accessed by diffusion along crystallographic cleavage planes.

The distribution of Cs was investigated using the electron (EMP) and X-ray (XMP) microprobes. In biotite, Cs was preferentially sorbed at the edges of broken platelets (Fig. 3a). This result supported the hypothesis that Cs is more strongly bound at edge sites, but did not address the (frayed or unfrayed) nature of those sites. Examination of sectioned biotite (Fig. 3b) also supported the hypothesis that internal sites can sequester Cs from solution.

Data from these studies are near the detection limit for the EMP method (note the granularity in the Cs image below). We are utilizing the X-ray microprobe technique (at the ANL synchrotron light source; e.g., Fig. 3b) to produce data with a higher compositional resolution to more fully evaluate our hypotheses; preliminary data from this method are at relatively low optical resolution, but show promise for detection of Cs with 100 times the sensitivity of EMP methods.

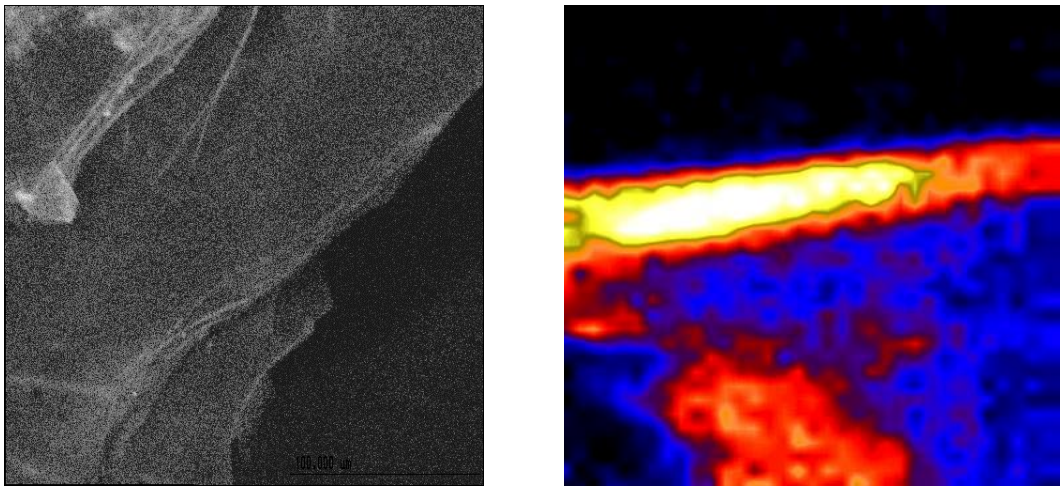

Figure 3. Adsorbed Cs^+ distribution maps for Hanford Site biotite exposed to a solution of 10^{-2} M Cs for 3 months. The left image is by EMP analysis of a plan-view specimen (200 micrometers across) and the right is by X-ray microprobe of a thin section (100 micrometers across). White intensity is proportional to Cs^+ concentration. Cs^+ is preferentially bound at platelet edges in plan-view (left image) and within internal, structural channels (right image).

Investigations of different micaceous minerals suggest that muscovite and vermiculite do not sorb Cs as strongly as biotite. Data to date are preliminary, and these results have not been confirmed.

4.) Identification of Cs-sequestering Minerals in Contaminated Hanford Sediments. Contaminated sediments from Hanford core 41-09-39 collected beneath Hanford Site storage tank SX-109 were examined to determine the relative abilities of different *in situ* minerals to bind and sequester Cs from leaked wastes. It is unlikely, given the physicochemical differences among these minerals, that Cs would be found to be evenly distributed across the different mineral species.

Sediment samples from several (closely spaced) depths beneath a leaked tank were assayed for Cs contamination using bulk chemical techniques. These sediments were then wet-sieved and size-segregated for further study.

We wished to optically identify mineral components of each size fraction and instrumentally determine the chemical association of Cs with dissimilar grains. Mineral grains from each size fraction were dispersed in a binding agent on glass slides. Optical examination showed some

mineralogic differences between size fractions, but in general the sediments consisted of primary silicate mineral grains, including abundant feldspars and micaceous minerals, along with secondary or detrital Fe oxides and clay minerals. After optical examination and preliminary mineral identification, mineral grain mounts were placed in a phosphorescence detector and incubated overnight. The detector stores gamma radiation chemically on a phosphor screen, allowing the detection and comparative quantitation of radiation from materials having relatively low activity. Exposure and digitization of phosphorescent images yielded radiation maps (autoradiographs) of dispersed particles, showing the relative abundance of Cs on mineral grains.

The comparison of mineral dispersions with radiation intensity maps allowed the identification of individual mineral grains having either "Cs positive" or "Cs negative" characteristics. New preparations were made from these mounts, in which twenty positive and twenty negative grains remounted in physically separate clusters. The "positive" and "negative" properties of the segregated grains were confirmed by repeating the radiation imaging step. This step allowed the direct determination of mineral phase identity for individual particles.

Mineral identities, primarily for "positive" grains but also for a minority of "negative" grains, were established using transmission electron microscopy (TEM) methods. Compositional information (collected using energy-dispersive X-ray spectroscopy) was collected in the microscope and combined with electron diffraction patterns captured on film. The combined data were used to search the JCPDS X-ray powder diffraction library for mineral identification (X-ray diffraction patterns are synthesized from electron diffraction data). Preliminary results indicated that Cs was not significantly bound to Fe oxides and non-phyllosilicates in these sediments. Cs was preferentially bound by

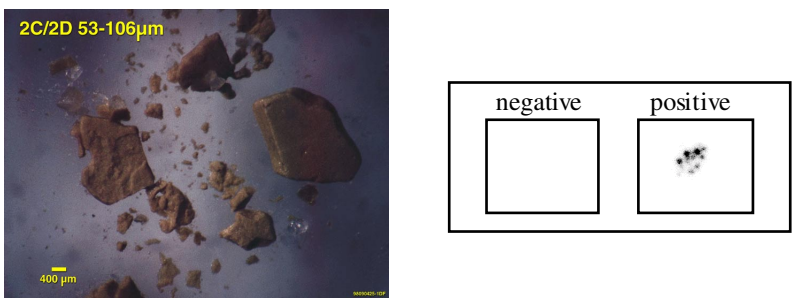

Figure 4. Optical image of segregated mineral grains (left), with final autoradiographic image (right) of segregated "positive" and "negative" particles. The darkness of autoradiographic spots indicates the radiation intensity; the clear area in the autoradiograph corresponds to grains that were "negative" for radiation. Clear, "negative" silicate grains are apparent in the optical image, as are "positive" phyllosilicate aggregates.

smectites and micas. These results have not been confirmed, and require additional experimentation to complete.

Our proximity to Hanford has allowed us to share our results with site remediation contractors that are developing closure plans for the Hanford tank farms where massive subsurface ^{137}Cs contamination exists. This information exchange has occurred through Hanford's Groundwater-Vadose Zone Integration Project. We have shown that Cs migration depth is strongly controlled by Na^+ concentration over its entire concentration range to saturation with $NaNO_3$. These observations and comparable ones with K^+ and Ca^{2+} electrolytes provide the basis for an improved mass-action model of Cs exchange-adsorption with Hanford sediments. Our desorption results from high sodium imply that a significant fraction of the sediment bound Cs becomes rapidly fixed and is not available for further migration. Further analysis of the desorption results and the performance of selected other experiments should allow firm guidance on whether in-ground Cs beneath the tanks can be left in place without environmental controls.

Planned Activities

The remainder of FY 99 activities will focus on the impacts of high base, variable temperature induced mineral dissolution on Cs^+ sorption in Hanford sediments and isolated mica fractions. We will identify whether the selectivity of the mica fraction for Cs^+ is changed by molar concentrations of hydroxide, and whether changes result from competitive ion effects (e.g., K^+ release by dissolution) or structural destabilization of the FES. The latter issue will be resolved by application of scanning probe microscopy and high-resolution transmission electron microscopy. In FY 00, similar studies will be performed using high-base waste stimulants containing $Al(OH)_4^-$ at concentrations that mimic those in the SST's. At issue is whether $Al(OH)_4^-$ precipitation that follows base neutralization will cause marked changes to Cs^+ sorption selectivity, kinetics, and reversibility. Important questions to be resolved include the nature of the precipitated Al-phase and whether it causes hydroxy pillaring and alteration of the structural environment of the FES. A combination of microscopy, solution phase thermodynamic measurements, and chemical modeling will be employed to interpret results and resolve hypotheses.

Publications and Presentations

Publications

Zachara, J.M., S.C. Smith, R.J. Serne, and P.L. Gassman. 1999. Highly selective Cs^+ adsorption by subsurface sediments from the Hanford site, U.S.A. Clays and Clay Minerals (Submitted).

McKinley, J.P., R.J. Serne, J.M. Zachara. 1999. Mineral phase association of Cs^+ in subsurface sediments contaminated with high-level nuclear waste. Environmental Science and Technology (Submitted).

McKinley, J.P, J.M. Zachara, and P.L. Gassman. 1999. Cs^+ distribution in natural micas: an electron and synchrotron X-ray microprobe study. Clays and Clay Minerals (In preparation).

Presentations

Zachara, J.M. New advances in the understanding of ^{137}Cs interactions with micas and implications to Cs geochemistry in the Hanford vadose zone. Keynote address given to the EMSP National Program Workshop, Chicago, Illinois. Aug. 1999.

Sorption of Heavy Metals and Radionuclides on Mineral Surfaces in the Presence of Organic Co-Contaminants

Project ID: 54860

Dr. James O. Leckie, Stanford University

Executive Summary

A review of the known inventory of chemical wastes at DOE facilities reveals that a large fraction of the waste is present as complex mixtures containing radionuclides, heavy metals, fuels, oils, organic solvents, and a variety of organic metal complexing agents (Riley and Zachara 1992). This situation is a result of a history of co-disposing wastes associated with chemical processing, metal surface cleaning, decontamination, and fabrication procedures used in the production of nuclear fuels and weapon components. Similar conditions also exist in industry where mixed wastes with heavy metals and chelating agents have been produced. The large inventory of complex and potentially unstable wastes must be stored until suitable treatment, confinement or disposal technologies have been developed. Unfortunately, in many cases the waste materials have been either discharged directly into open pits, or have since escaped from temporary containment facilities and now contaminate surrounding soils and groundwater.

The chemical complexity of these wastes present particularly challenging problems with respect to predicting subsurface migration of the radionuclides and heavy metals, and developing suitable remediation strategies. Among the organic compounds at DOE sites are a number of organic chelating agents that can form stable solution complexes with metals, radionuclides, and their oxy-ions. Examples include ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and citric acid. It would be reasonable to predict that the formation of metal-organic complexes, especially those with stable multi-dentate structures, will influence the mobility of the metals and radionuclides in soils and groundwater. A general prediction that is consistent with the few available field studies would be that metal complexing organic ligands should increase metal mobility. This has already been demonstrated in a number of studies (e.g., Means et al., 1978; Girvin et al., 1993; Zachara et al., 1995). However, recent work with uranium and citric acid (Redden et al., 1996) and cadmium and citric acid (Boily and Fein, 1996) on metal oxides has shown that, under particular chemical conditions, complexing agents can actually enhance metal adsorption. Mobility of ionic solutes in groundwater is a function of the extent of partitioning between the mobile (water) and immobile (soil, mineral) phases. Organic ligands compete with reactive surface binding sites for metal solutes, or bind directly to surfaces thereby altering the type and availability of binding sites. In most field applications, increased mobility of soil and groundwater contaminants is not desirable since retrieval of the contaminants or isolating the public from hazardous conditions becomes more difficult as zones of contamination expand. However, in some cases, where remediation involves contaminant recovery, maximum mobility can be a distinct advantage.

At present, with the available experimental database, broad generalizations concerning the effect of organic ligand and chelating agents on metal or radionuclide mobility cannot be made. The quantitative predictions of partitioning that are necessary to estimate contaminant transport are not yet possible, and specific details of the chemical mechanisms are still hypothetical. In order to make reasonable transport predictions, an expanded database is needed for a range of priority heavy metal contaminants, common ligands, and representative mineral surfaces. Elucidating the mechanisms by which organic ligands affect metal partitioning at surfaces will provide information necessary for the design of effective treatment strategies.

Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases

Project ID: 70081

Dr. Samuel J. Traina, Ohio State University

Dr. Gordon E. Brown, Jr., Stanford University
Dr. Philip Grandinetti, Ohio State University
Dr. Calvin C. Ainsworth, Pacific Northwest National Laboratory
Dr. Jim E. Szecsody, Pacific Northwest National Laboratory

Executive Summary

The production and extraction of Pu, U and other strategic elements from irradiated uranium fuels has been a major component of the DOE mission since the early 1940's. At the Hanford site, the fluids resulting from extraction of spent fuel rods from 9 nuclear reactors were stored in 177 underground tanks during the period of 1944 to 1990, in areas known as "tank farms". The chemical extraction processes employed at the Hanford site ultimately produced hyperalkaline, high level waste (HLW) fluids that were stored in underground tanks. Many of these contained large concentrations of $NaNO_3$ (often > 1 mol L^{-1}) and hydroxyl ions, with pH values > 10 common and some in excess of 14, large concentrations of dissolved Al (which presumably stayed in solution as aluminate ions and possibly aluminate polymers) quantities of unrecovered U and Pu, numerous fission daughter products, organic ligands (from the extraction and purification processes), and a number of other inorganic ions.

Sixty-seven of the single shelled tanks are known or thought to have leaked, allowing from 1,920,000 to 3,456,000 L of waste fluids to migrate into the underlying vadose zone. The actual composition of these leachates is not fully known but the existing data, indicate that many of these fluids were highly alkaline (pH values > 13), and that many contained large concentrations of dissolved $NaNO_3$ and $Al(OH_4)^-$ as well as substantial quantities of ^{137}Cs, ^{60}Co, ^{90}Sr, ^{99}Tc, $^{234,238}U$, and other radioactive elements. Upon reaction with the underlying soil and sedimentary matrix this situation will potentially result in the formation of a number of complex precipitates that could incorporate radioactive contaminant species from the tanks. Reaction of the tank fluids with the soil matrix will cause some dissolution of the soil minerals, releasing Si into solution, and decreasing pH. These solution conditions promote the formation of Al- and Si-hydroxide gels, hydrotalcites, Al-(hydr)oxides zeolites and other secondary phases. All of these potential phases have high surface reactivities, and should serve as strong sorbents and/or coprecipitates for contaminant ions present in the leachate (Cs, Co, Sr, Tc, U, etc.). Additionally, partial dissolution of the ambient soil minerals and precipitation of these secondary solids could result in significant alteration to the porosity and flow paths of the surrounding porous media. When coupled together, these chemical and physical transformations should result in dramatic changes in the fate and transport of the contaminant ions associated with tank fluids. Clearly, more information is needed before an understanding of the complex geochemical environment in the vadose zone beneath the Hanford tanks is attained.

In this three-year collaborative project, we are studying the incorporation of representative contaminant species (Cs, Co, Sr, Tc, and U) in carefully controlled model systems to gain a more fundamental understanding of sorption, neoformation, precipitation, and exchange processes that might immobilize these contaminants in solid matrices impacted by alkaline tank fluids. This activity will provide mechanistic information on many of the geochemical processes occurring beneath the HLW tanks. Additionally we will directly measure the solid-phase speciation of a number of contaminants from sediment samples obtained from directly beneath suspected, leaking HLW tanks.

This data will be critical in the ongoing efforts to predict radionuclide transport and stability in subsurface zones at Hanford that have been impacted by tank waste. It will also be critical in assessing the potential for remobilization of any subsurface contamination by accidental spills that may occur during current and future remediation activities at Hanford, such as the possible sluicing and of solids within the HLW tanks.

Research Objectives

We are investigating (1) the effect of aging on the stability of sorption complexes (of Cs, Co, Sr, Tc, and U ions) on Al-oxide and Al-oxyhydroxide surfaces formed from neutralization and homogeneous nucleation of alkaline aluminate solutions; (2) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with simple systems of representative minerals and mineral coatings found in the soils and sediments underlying the Hanford Tank Farm (e.g., quartz, feldspars, biotite, muscovite, chlorite,clay mineral, augite, hornblende, ilmenite, magnetite, hematite, Fe(III)-oxyhydroxides, and Mn(IV)-(hydr)oxides); and (3) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with soil and sediment samples obtained from the Hanford site. These latter experiments will be conducted in batch as well as flow through systems(4). To couple these laboratory studies to precipitation processes occurring in the Hanford vadose zone beneath the Tank Farm, we will characterize the particle coatings and precipitate phases in contaminated core samples from this zone. These investigations will utilize X-ray Absorption Fine Structure (XAFS) spectroscopy, vibrational spectroscopy, NMR spectroscopy, electron and X-ray microprobe analyses, transmission electron microscopy, X-ray photoelectron spectroscopy, and other characterization studies of the speciation and spatial distribution of these ions in several model systems chosen to simulate the natural systems as well as contaminated sediments from the sites.

Research Progress and Implications

This project formally began in the fall of 1999. Since that time we have: 1) developed detailed experimental protocol, 2) identified and obtained specimen mineral samples as well as uncontaminated sediment samples from the Hanford site, 3) initiated batch sorption experiments with Co, Sr, and Cs, in HLW tank simulant solutions, 4) initiated long-term aging studies, and 5) begun initial XAFS studies of these systems.

Modeling of Cation Binding in Hydrated 2:1 Clay Minerals

Project ID: 54823

Dr. David E. Smith, New Mexico State University

Research Objective

The primary objective of our research is the development of molecular models of ion exchange on clay minerals with a view toward understanding the mechanisms of radionuclide transport through clay-rich soils. Specific scientific goals include using molecular computer simulations to calculate the thermodynamics of clay swelling and ion exchange, and to evaluate the dependence of clay properties upon interlayer ion identity and clay composition. These goals will, in general, facilitate the development structure-function relationships in clays.

Research Progress and Implications

This report summarizes work completed in the first 2.75 years of the 3-year project period, with emphasis placed on the most recent accomplishments.

Method and Code Development: This phase of the project was essentially completed with the recent development of a grand-canonical ensemble molecular dynamics (GMD) simulation method.[1,2] Ion exchange and clay swelling processes in the environment typically take place under conditions of constant water chemical potential. These conditions are reproduced in the GMD simulations. Particle insertion and deletion processes, made difficult by the constrained clay interlayer environment, are catalyzed using a bias potential method developed by us.

Swelling Free Energy: The GMD method has been applied to investigations of the swelling of Cs-montmorillonite[2] and Na-montmorillonite[3] in contact with bulk water. Disjoining pressures at constant water chemical potential were calculated as a function of clay layer spacing over a region encompassing the one- and two-layer hydrates. The pressures show oscillations that are indicative of crystalline-swelling phase transitions. Integration of the disjoining pressures yielded free-energy curves with minima at approximately 12.5 (Cs only) and 15.5 Å, representative of the one-layer and two-layer hydrates. These are displayed in Fig. 1. Results for Cs-montmorillonite indicate incorrectly that the two-layer hydrate is more stable than the one-layer hydrate.[4] The simulation model may therefore require some adjustment for quantitative treatment of clay swelling. Decomposition of the free energy into its entropic and energetic components indicates that the one-layer hydrate is favored energetically, but disfavored entropically. The dependence of the swelling free energy upon ion size is qualitatively correct. While results for sodium-montmorillonite should be considered preliminary, decreasing the interlayer ion size clearly results in stabilization of the two-layer hydrate relative to the one-layer hydrate.

Ion Exchange: Ion exchange calculations are being performed using a method that isolates the constant-volume exchange and swelling contributions to the overall exchange process. Sodium to cesium exchange free energies, calculated at constant layer spacing for a montmorillonite clay, have been determined at several water contents. These results were discussed in a previous report. The swelling contribution to exchange may be calculated from the GMD swelling free energies displayed in Fig. 1. Exchange of sodium with cesium is much more favorable for the one-layer hydrate than for the two-layer hydrate. This is in agreement with the experimental observation that exchange with cesium is accompanied by dehydration to the one-layer hydrate. [4] The overall exchange free energy is also qualitatively consistent with experimental measurements.[5]

Ion Size and Charge Dependence: The ion size and charge dependence of clay swelling has been investigated using Na, Cs, and Sr-montmorillonite clays.[6,7] Results suggest a dramatic difference in behavior between monovalent- and divalent-ion substituted clay minerals. Immersion energies for the three clays are displayed in Fig. 2. All three curves show oscillations consistent with a discrete swelling mechanism. The results indicate, in agreement with experiment,[4] that the one- layer hydrate is energetically favored for Cs-montmorillonite, while the two-layer hydrate is favored for both Na- and Sr-montmorillonite. The immersion energy curve for Sr-montmorillonite shows a discontinuous jump at approximately the one-layer hydrate. The energetic jump is accompanied by significant increases in clay layer spacing and in the strontium coordination number. Metastable states occur along both branches of the immersion energy curve surrounding the discontinuity. This suggests that, for Sr-montmorillonite only, there is a constant water content phase transition between one-layer and two-layer spacings. This transition has been characterized using pressure versus layer spacing isotherms. Integration of the isotherms yields a free-energy curve with minima for both one- and two-layer states. This has provided the identification of global free-energy minima for several

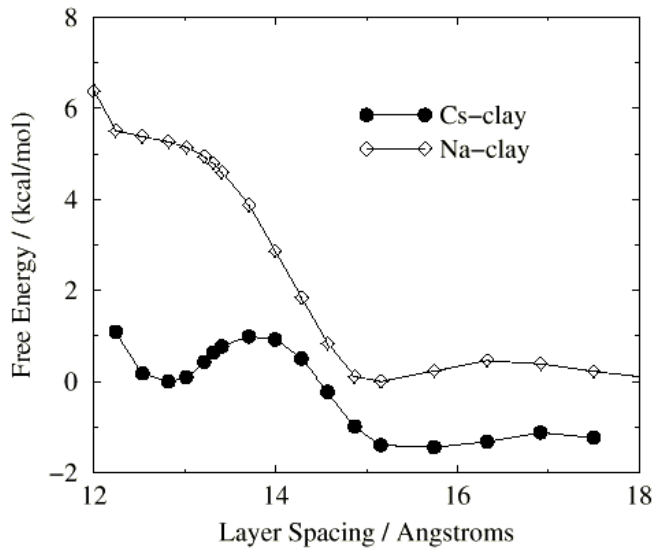

Figure 1: Swelling free energies. Curves are displaced for clarity.

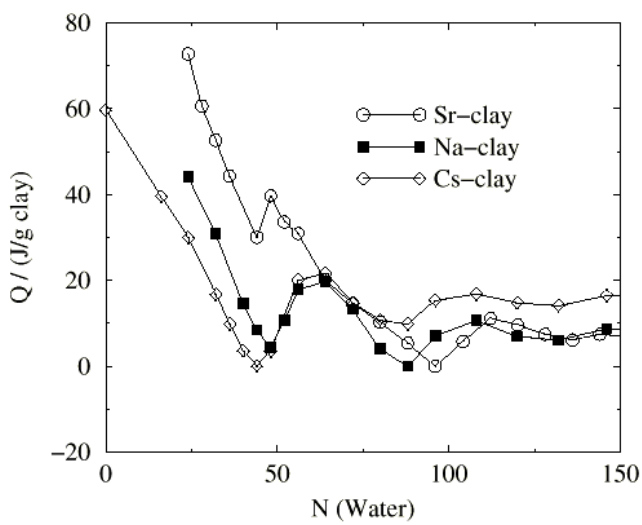

Figure 2: Immersion energies.

water contents near the transition point. The discontinuous behavior in Sr- montmorillonite possibly originates from the strong, Sr-water interactions that force the clay to two-layer spacings even with near one-layer water contents.

Planned Activities

A one-year, no-cost extension for this project has been requested. This will allow for expansion of the breadth of the ion exchange and swelling calculations discussed above to include a wider range of interlayer ions and clay composition. This is necessary for the evaluation and development of ion exchange models. Efforts to address some simulation model deficiencies will also be made.

References

1. R.M. Shroll and D.E. Smith, J. Chem. Phys. **110**, 8295 (1999).
2. R.M. Shroll and D.E. Smith, "Molecular Dynamics Simulations in the Grand Canonical Ensemble: Application to Clay Minerals" (in preparation).
3. R.M. Shroll, D.A. Young, R. Waymire, and D.E. Smith, "Computer Simulations of Ion Exchange in Clay Minerals" (in preparation).
4. I. Bérend, J.-M. Cases, M. Francois, J.-P. Uriot, L. Michot, A. Masion, and F. Thomas, Clay & Clay Miner. **43**, 324 (1995).
5. S. Xu and J.B. Harsh, Soil. Sci. Soc. Am. J. **54**, 1596 (1990).
6. D. E. Smith, Langmuir 14 , 5959 (1998).
7. D.A. Young and D.E. Smith, "Ion Size and Charge Dependence of Clay Mineral Swelling" (in preparation).

Information Access

References [1] and [6] above are in print. A topical report for each article will be submitted shortly. Reference [2] has a target submission date of June 30th, reference [7] of July 31st, and reference [3] of September 30th.

Reactivity of Primary Soil Minerals and Secondary Precipitates beneath Leaking Hanford Waste Tanks

Project ID: 70070

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R. Jeff Serne, Pacific Northwest National Laboratory
Steven B. Yabusaki, Pacific Northwest National Laboratory

Research Objective

Since the late 1950s, leaks from 67 single-shell tanks at the Hanford Site have released about 1 million curies to the underlying sediments. There is a risk that future remediation activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone. At issue is the distribution of contaminants beneath the tanks, and the processes that led to their current disposition and will control their future mobility. The high ionic strength, high pH, and high aluminum concentrations in the tank liquids can significantly alter the vadose zone sediments through dissolution of primary minerals and precipitation of secondary minerals. Dissolution and precipitation directly influence (1) the flow paths that control contaminant transport and (2) the reactivity of the solid matrix that controls contaminant mobility. The impact of these processes, however, depends on mineral reaction kinetics and the dynamic interaction of the reactions with the flow field and contaminant sorption, neither of which are well-known for this extreme chemical system. Precipitation of Al-hydrous oxides is expected as tank solutions mix with ambient Hanford soils and solutions. Depending on the mixing conditions, stable or metastable phases might precipitate, while reaction rates will depend on the kinetic factors of temperature, solution composition, and reactive surface area. Polymeric Al-species may precipitate as colloids, and adsorb to other minerals or be transported in solution. Dissolution of primary minerals will provide components that can reprecipitate with Al as clays, zeolites, or layered double hydroxides. Sorption and desorption of radionuclides will be a function of the amount of surface area of the neoformed phases and may fluctuate as the amounts of these reactive phases vary with changes in the ambient environment. Data obtained will be directly useful to other EMSP projects addressing contaminant mobility in the vadose zone.

We intend to address three specific issues:

(1) Recognized factors that control the kinetics of dissolution and precipitation must be quantified for the unnatural system of tank solutions mixing with soils, including effects of high pH, high ionic strength (especially $NaNO_3$ solutions), temperature, and saturation state.
(2) A clear understanding of the roles of nucleation mechanism, nucleation sites on soils minerals, and the role of reactive surface area in simultaneous dissolution and precipitation reactions are the key unknown components in comprehending this contaminated soil system.
(3) Results obtained in (1) and (2) will help build a mechanistic understanding of how tank fluids migrate through the vadose zone. Local changes in porosity and permeability will dictate preferential flow paths which directly regulate the transport of later arriving chemical species. Changes in mineral surface area affect sorption site distribution. A comprehensive model is needed that integrates these feedback mechanisms with all the critically available data.

Research Progress and Implications

The goal of the first phase of the project is to obtain kinetic rate laws to describe the dissolution of quartz and feldspar, as well as the precipitation of secondary phases, as high pH, high ionic strength,

high aluminum fluids come into contact with the primary phases. This work involves fundamental kinetic measurements conducted at the University of Colorado, and saturated column experiments at PNNL. Preliminary column experiments using quartz and Hanford sediment, and 0.3 and 3 m NaOH have been conducted at PNNL. At Colorado, work has commenced as of January 2000 on three fronts: sample collection and characterization, thermodynamic calculations, and experimental design.

High purity, natural quartz sand and synthetic gibbsite have been obtained. Quartz will be examined as a primary dissolving mineral, whereas gibbsite will be used to obtain solutions in equilibrium with respect to that phase under the conditions of interest as well as examined for its own dissolution and precipitation kinetics. In order to purify the quartz, we have used magnetic separation and sustained treatment with sulfuric acid. Quartz surfaces will be further conditioned by treatment with boiling deionized water. The purity of the bulk quartz sample and the quartz surfaces before and after the various treatments are being assessed by X-ray Fluorescence Spectroscopy and Auger Electron Spectroscopy, respectively. Gibbsite was X-rayed to determine its purity, and particles < 10 μm in diameter were removed via size-settling in low pH, low ionic strength solutions. Size separation was verified using Scanning Electron Microscopy.

We modified one of the thermodynamic databases in the Geochemist's Workbench geochemical modeling software to account for Pitzer ion interaction parameters relating to the aqueous Al species of interest in our experimental systems and their interactions with Na. Calculations fairly accurately reproduce published gibbsite solubility data. Pitzer coefficients for $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ have also been included at 25°C, and we are working on approximating temperature-dependent coefficients for these Si species. If polynuclear Si species need to be considered at higher pHs, we will approximate activity coefficients within the Pitzer formalism starting by refitting activity coefficients calculated using SIT (specific-interaction-theory).

Most of the equipment needed to run the initial kinetic experiments has been obtained. We have designed protocols to minimize interference from carbonate species, and to obtain unambiguous kinetic data. We expect to start the kinetics experiments within one month.

Planned Activities

At Colorado, the kinetic experiments will be conducted in two stages. Batch experiments will be used to make a first assessment of kinetic rates and reaction products. Given the approximate rates obtained from the batch experiments, single-pass stirred-flow reactor experiments will be performed to more tightly constrain rates as functions of saturation state, solution composition, and temperature. Experiments will be performed from 25 to 90ºC, and from pH 9-14 in 0 and 2 m $NaNO_3$, with pH adjusted by titrating with NaOH. Batch experiments will be started within one month and stirred-flow reactor experiments within three months. Analysis of the column experiments conducted at PNNL will be completed within four months. Such analysis will include rate calculations based on measured effluent Si and pH; characterization of the solids with X-ray diffraction and selective extraction of amorphous precipitates; and, determination of changes in saturated hydraulic conductivity, moisture retention, and particle size. Subsequent kinetic work will be determined based on the initial results from all sets of experiments.

Aquifer Transport of Th, U, Ra, and Rn in Solution and on Colloids

Project ID: 55284

Dr. G. J. Wasserburg, California Institute of Technology

Mahalingam Baskaran, Texas A&M University

Research Progress and Implications

We have completed a theoretical study of the U-Th and radioactive decay series in an aquifer. Using this model as a guide, we have reassessed our results on the aquifer associated with Brookhaven National Laboratory. Based on our study and analyses of the U-Th series nuclei in this aquifer and the theoretical results, it was considered mandatory that a new set of samples be acquired. In addition to data from the groundwater samples, information concerning the addition of nuclides into the ground water system from the vadose zone was needed. A field study was then carried out and the samples returned to the laboratory. Sampling was done in consultation with hydrologists from the Brookhaven National Laboratory staff. The analyses are now almost completed and a draft of the final report is in preparation.

Unfiltered, filtered and ultra-filtered water samples were collected to determine the role of particles and colloids in the transport of radio-nuclides. Data were obtained on ^{238}U, ^{234}U, ^{232}Th, ^{234}Th, ^{226}Ra, ^{222}Rn, ^{228}Ra and ^{224}Ra. In addition, chemical analyses were carried out for the standard dissolved load. It was found that there has been an addition of Cl into the ground waters from the surface.

The results show that the waters in the upper glacial aquifer are intruded at some locations by waters from the underlying Magothy unit. The relative effects of U addition to the groundwater from alteration in the ground water table itself as compared to the contributions from the vadose and soil zones was investigated. It was found that a substantial to dominant contribution of U in the groundwater comes from the vadose zone. The "dissolved" U in the groundwater is, in several cases, governed by the presence of colloids. It would appear that the variable concentration of ^{238}U along nominal flow lines is due in part to non-conservative behavior involving precipitation and dissolution of colloids. The data indicate that there are both removal (i.e., precipitation mechanisms) available even under oxidizing conditions. Also sharp changes in both the concentration and isotopic composition (^{234}U/^{238}U) occur due to the dissolution of some phases within the groundwater table. The colloids show distinct differences in ^{234}U/^{238}U relative to the dissolved load and show there is not rapid exchange between these components. It appears the U in the dissolved load <10 KD.

The nominal hydrologic flow lines that were used as the basic guide to the original sampling do not appear to represent the actual flow lines. We consider this to be the more plausible hypothesis. This implies that the transport in an aquifer where the "age" of the water is young ($\leq 2 \times 10^2$ years) is governed by the precise details of the flow from the vadose zone into the aquifer for considerable distances. Any "diffusive" mixing over this distance (time) scale is thus inadequate to smooth gross irregularities from local sources in the soil weathering zone. Percolation appears to be an important to dominant process. The final data sets are now being acquired and a final report will be completed with the next six months.

Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions

Project ID: 70177

Nancy J. Hess, Pacific Northwest National Laboratory

Steven D. Conradson, Los Alamos National Laboratory

Research Objective

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

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

Research Progress and Implications

This report summarizes work after 6 months of a 3-year project. We have made limited progress in the areas of TcO_2(am) solubility studies. TcO_2(am) was prepared from pertechnetate stock solution by hydrazine and microbial reduction using the subsurface dissimilatory iron-reducing bacterium, *Shewanella Putrefaciens*. The amorphous product prepared by both methods was characterized by x-ray absorption spectroscopy and x-ray diffraction. In Figure 1, the near edge structure of the x-ray absorption spectra indicates complete reduction of Tc^{VII} to Tc^{IV} by either method. Note, however, that the amplitude of the x-ray absorption fine structure of the microbially reduced TcO_2(am) is significantly greater than the hydrazine reduced TcO_2(am). This is especially evident in the k^3-weighted EXAFS spectra shown in Figure 2 and in the Fourier transforms of the EXAFS spectra shown in Figure 3. Fits to the EXAFS indicates that the first and second shells in the Fourier transform correspond to oxygen and technetium atoms, respectively. The decreased EXAFS amplitude of the hydrazine reduced TcO_2(am) may result from increased static disorder; however this needs to be confirmed by additional experiments.

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

Planned Activities

The solubility of TcO_2(am) and possible Tc^{IV}-Fe^{III} oxides will be measured as a function of pH under rigorously controlled redox conditions. The oxidation state of Tc in solution will be determined by a variety of methods, such as solvent extraction techniques, laser photoacoustic spectroscopy (LPAS), UV-Vis-NIR spectrophotometry, and x-ray absorption near edge structure (XANES) analysis. The methods used will depend on the concentration of Tc in solution. Solvent extraction and LPAS will

Figure 1

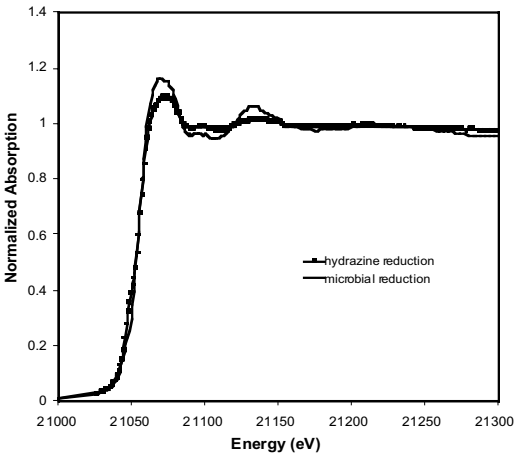


Figure 2

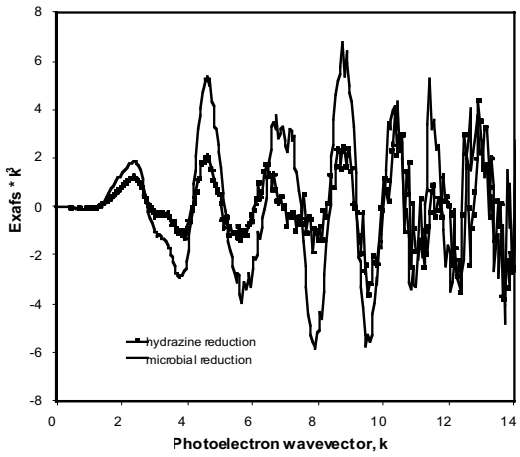


Figure 3

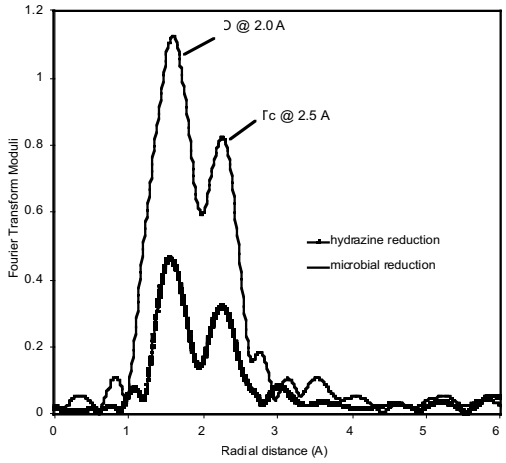
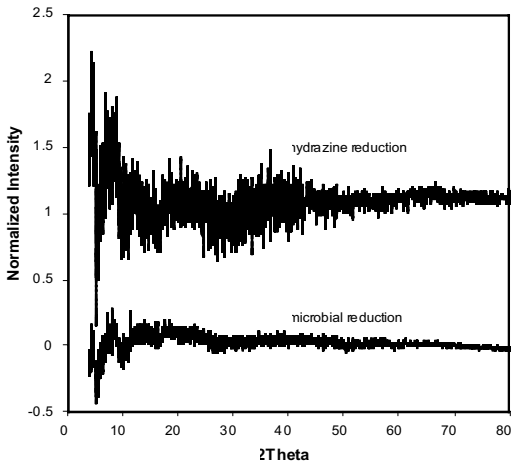


Figure 4



provide oxidation state information at the lowest Tc concentrations, approximately 1 x 10^{-9} M. The solvent extraction process requires acidification of the sample that can potentially change the oxidation state. On the other hand, LPAS requires no alteration to the solution chemistry and distinguishes between the reduced Tc oxidation states. But LPAS is very time intensive. The detection limits for UV-Vis-NIR spectrophotometry and XANES analyses are approximately 1 x 10^{-6} M and 5 x 10^{-4} M, respectively.

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

Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria: In-Situ Radionuclide Transport and Preferential Groundwater Flows at INEEL (Idaho)

Project ID: 54741

Michael Murrell, Los Alamos National Laboratory

Teh-Lung Ku, University of Southern California
Shangde Luo, University of Southern California
Robert Roback, Los Alamos National Laboratory

Research Objective

The Idaho National Engineering and Environmental Laboratory (INEEL) is a Department of Energy facility that encompasses approximately 2300 km^2 in the west-central part of the Eastern Snake River Plain. Since the early 1950s, low-level radioactive and non-radioactive waste was disposed of via injection wells that penetrate to the aquifer. Contaminant plumes extend downgradient from these injection wells and some contaminants can be tracked to near the southern boundary of the site. In addition, there are several surface and shallowly buried waste storage sites that have released contaminants to the environment. Concerns about existing and potential additional contamination of the aquifer have prompted numerous studies to better understand groundwater flow and contaminant migration in the aquifer. This research is directed toward an assessment of rates of the water-rock-radionuclide interactions, the preferential groundwater flow paths, and the transport of radionuclides in fracture-rock systems using a natural analog approach. It falls under one of the five focused topical areas of the ER/EM Collaborative Research Program (Topic 1 of the ER/EM Collaborative Research Solicitation: September 1995).

The goal of the research is to study the migration of nuclear waste contaminants in subsurface fractured systems using naturally occurring uranium- and thorium-series radionuclides as tracers under in-situ physico-chemical and hydrogeologic conditions. We develop a model of contaminant migration in the Snake River Plain Aquifer beneath the INEEL by evaluating the retardation processes involved in the rock/water interaction. The major tasks are to determine: (1) the distribution of U, Th, Pa, Ra, Rn, Pb and Po isotopes in groundwater as well as in rock minerals and sorbed phases, (2) through modeling the extent of disequilibria the in-situ retardation factors of radionuclides and rock/water interaction time scales, and (3) the water residence time in the aquifer and the preferential flow paths. The study provides an improved characterization of preferential flow and contaminant transport in fractured rocks — information that pertains to risk and performance assessment and remediation action at INEEL and other contaminated DOE sites.

Research Progress and Implications

The project is a collaborated research between the University of Southern California (USC) and the Los Alamos National Laboratory (LANL). Studies performed at USC include the measurement of U, Th, Ra, Rn, Pb, and Po radionuclides by decay-counting techniques and the modeling of the migration behaviors of these radionuclides.

We have developed an in-situ filtration-enrichment sampling system to obtain groundwater samples sufficiently large to allow measurement of the short- as well as long-lived nuclides of the U and Th

decay chains. It was successfully deployed to collect groundwater samples of ~1000 liters from 23 wells from INEEL. Isotopes of uranium (^{238}U, ^{234}U), thorium (^{232}Th, ^{230}Th, ^{228}Th, ^{234}Th), radium (^{226}Ra, ^{228}Ra, ^{224}Ra), polonium (^{210}Po), and lead (^{210}Pb) were pre-concentrated in the field by passing ~1000 liters of groundwater through two cartridge filtration units (connected in series) containing MnO_2-impregnated acrylic fiber adsorbers. Small-volume samples were collected for ^{222}Rn measurements by the radon emanation method using alpha-scintillation counting. Three field sampling trips were completed during the first two years of the project. We have accomplished most of the analyses on the groundwater samples (except for ^{210}Pb whose activities are determined through ^{210}Po ingrowth which requires about one year's time after separation of Pb from the samples), and have thus far obtained data on a range of wells from the site to allow the following summary of results.

The results show that groundwater activities of Th and Ra isotopes are 2-4 orders lower than those of their U progenitors which average 1.35±0.40 dpm ^{238}U/L, with $^{234}U/^{238}U$ ratios of ~1.6–3.0. ^{222}Rn activities range from 20 to 500 dpm/L. Modeling of the observed disequilibria places the following constraints on the time scale of radionuclide migration and water-rock interaction at INEEL: (1) Time for sorption is minutes for Ra and Th; time for desorption is days for Ra and years for Th; time for precipitation is days for Th, years for Ra, and centuries for U. (2) Retardation factors due to sorption average $>10^6$ for ^{232}Th, $\sim10^4$ for ^{226}Ra, and $\sim10^3$ for ^{238}U. (3) Dissolution rates of rocks are ~70 to 800 mg/L/y. (4) Ages of groundwater range from <10 to 100 years. Contours of groundwater age, as well as spatial patterns of radionuclide disequilibria, delineate two north-south preferential flow pathways and two stagnated locales. Relatively high rates of dissolution, precipitation, and α-recoil of ^{222}Rn occur near the groundwater recharging sites and in the major flow pathways. Decay of the sorbed parent radionuclides (e.g., ^{226}Ra and ^{228}Ra) on micro-fracture surfaces constitutes an important source of their daughter (^{222}Rn and ^{228}Th) activities in groundwater.

This study, by providing for the first time a comprehensive and quantitative assessment of the in-situ migration rates of radionuclides in the groundwater of a DOE site, shows that the naturally-occurring decay-series isotopes in groundwater are uniquely suited for study of site-specific, long-term transport of nuclear wastes in the groundwater. The study reveals the importance of dissolution and precipitation in controlling the transport of radionuclides in groundwater which are difficult to ascertain through lab experiments. Recognizing the role of a sorbed pool of radionuclides in aquifer rocks by this study cautions us in the use of batch experiments to determine distribution coefficients of radionuclides, as many of the surface sorption sites on rocks are formed in nature over geological time scales.

Information Access

Copies of the following publications are available from USC.

Ku T. L., Luo S., Leslie B. W., and Hammond D. E. (1998) *Radiochimica Acta*, **80**, 219-223.

Luo S., Ku T. L., Roback R., Murrell M. T., and McLing T. (2000) *Geochim. Cosmochim. Acta*, **64**, 867-881.

Luo S., Ku T. L., Roback R., Murrell M. T., and McLing T. (in press) in: *Scientific Basis for Nuclear Waste Management XXIII, proceedings vol. 608 of the Materials Research Society Symposium Proceedings Series.*

E-prints: http://emsp.em.doe.gov/eprint.htm

Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in Soils and Vadose Zone Sediments

Project ID: 70146

Dr. Richard J. Reeder, SUNY at Stony Brook

Research Objectives

The release and migration of toxic metals and radionuclides in the soil and vadose zones at various sites over the DOE Complex pose serious technological challenges, including the design and implementation of cost-effective remediation strategies. This requires knowledge of the factors that govern contaminant mobility and reactivity within their host materials. Pedogenic calcium carbonate is a locally important component of soils and vadose-zone materials at the Hanford Site, where it coats grains and occurs as a massive caliche layer at depth. This project examines the reactions and uptake behavior of toxic metals and radionuclides present in soils and vadose-zone sediments containing calcium carbonate.

The main research objective is to assess the effectiveness of uptake and retention of selected contaminants (Co, Cs, Pb, Sr, and Cr) on calcium carbonate (calcite), with a focus on conditions and materials relevant to the Hanford Site. This includes detailed microscopic and spectroscopic characterization of carbonate coatings and caliche from the Hanford Site, combined with experimental determination of the uptake behavior of selected contaminants on calcite surfaces and consideration of factors influencing uptake behavior and retention. This will rely on microscopic, mineralogical, and geochemical characterization of natural materials, as well as spatially resolved X-ray fluorescence (micro-XRF) and X-ray absorption fine structure (XAFS) spectroscopy of uptake products. The expected results will have direct application for assessing the role that calcium carbonate phases play in sequestering toxic metals and radionuclides at the Hanford Site.

Research Progress and Implications

This section summarizes work completed after 6 months of a 3-year project. Preliminary findings relate to two specific areas: coprecipitation of CrO_4^{2-} with calcite and reaction of Pb^{2+} and Sr^{2+} containing solutions with natural caliche samples from the Pasco Basin area. These findings are necessarily preliminary in nature. Controlled laboratory coprecipitation of CrO_4^{2-} with calcite shows that CrO_4^{2-} is discriminated against during crystallization, i.e., the $K_d < 1$ for CrO_4^{2-} incorporation with calcite. Experiments on calcite single crystals, however, reveal a strong surface control on K_d. In particular, the distribution and availability of different surface sites on calcite, results in differences in uptake that may be as large as a factor of 5. This suggests that the nature of the carbonate surface plays an important role in the extent to which CrO_4^{2-} is removed from soil and vadose-zone fluids when calcite is forming. Current work assesses the role of crystallization rate on uptake behavior.

Experiments have also been initiated to assess the interaction of Pb^{2+} and Sr^{2+} containing solutions with natural caliche from selected locations in the Pasco Basin area. These caliche samples share many characteristics with those found in Hanford Site sediments. Initial results indicate a strong but spatially heterogeneous interaction of Pb^{2+} with calcite. This suggests that only a small proportion of the caliche surface offers favorable reactive sites for Pb^{2+} uptake. Current work is aimed at characterization of the mechanism of uptake. Sr^{2+} interaction is also observed, but the presence of Sr in the caliche complicates characterization. Further work is underway to address these problems.

Planned Activities

Future activities call for both adsorption and coprecipitation studies of selected metal species with calcium carbonate. Systematic adsorption and desorption behavior will be studied using radiolabeled metals and gamma spectroscopy. X-ray absorption fine structure (XAFS) spectroscopy will be used to characterize the local coordination of metal species during and following uptake experiments. Spatially resolved X-ray fluorescence and X-ray absorption spectroscopy (micro-XRF/XAS) will be used to map the distribution of contaminant reaction products after exposure to natural carbonate substrates in parallel experiments. Separate coprecipitation experiments with selected contaminant metals will allow an assessment of the effectiveness of uptake during crystallization of calcite, which may be favored in the soil and vadose zone as a result of periodic wetting and drying, and also in response to the highly alkaline waste fluids. XAFS spectroscopy will again be used to confirm speciation with the solid calcium carbonate.

Sorption of Colloids, Organics, and Metals onto Gas-Water Interfaces: Transport Mechanisms and Potential Remediation Technology

Project ID: 55396

Dr. Jiamin Wan, Lawrence Berkeley National Laboratory

Research Objectives

The purpose of this project was to explore and refine applications of isotope ratio measurements for guiding environmental remediation strategies. The isotopic compositions of samples collected from field sites were analyzed to address both basic scientific issues and site-specific problems.

Research Progress and Implications

This report summarizes the primary results of a 3-year project. Initial efforts were concentrated on two sites at the Idaho National Engineering and Environmental Laboratory (INEEL). During the final year of the project, the focus of work was shifted to the Hanford site in Washington.

The Test Area North (TAN) site at INEEL consists of a 2 km-long plume of mixed wastes containing low-level radionuclides, sewage and chlorinated solvents that were injected into the groundwater between 1955 and 1972. Measurements were made of the hydrogen, carbon, oxygen and strontium isotopic ratios of groundwater samples to address questions about the source of the groundwater and the regional hydrology of the area. These data indicate that there is a significant input to the groundwater from playa lakes that were located to the west of the TAN site (these playas have been dry since the 1950s when the water that fed the playas was diverted for agricultural uses). This playa water strongly influences the direction of groundwater flow in the TAN plume.

Another goal of the work at the TAN site was to evaluate the level of intrinsic biodegradation of the contaminants in the plume. Mixing of the playa water with regional groundwater has produced a range of strontium isotopic compositions in the plume that can be used to estimate the degree of dilution of the injected wastewater. Relative to the changes in strontium isotope ratios, the concentrations of TCE in the plume decrease more rapidly, indicating that natural biodegradation of the TCE is occurring at the site. This finding is supported by a decrease in the carbon isotope ratio of dissolved inorganic carbon compounds (DIC) in the plume. Organic compounds, such as TCE, have low carbon isotope ratios that will be reflected in the carbon isotope ratios ($\delta^{13}C$) of DIC produced as a byproduct of biodegradation. During FY99, the work on the TAN plume was expanded to help monitor an experiment designed to enhance biodegradation of the TCE in the plume. In addition to tracking changes in the $\delta^{13}C$ values of the groundwater DIC, the $\delta^{13}C$ values of the contaminants and biodegradation byproducts were also analyzed. These data confirmed that complete biologic dechlorination of the TCE was being stimulated by the nutrients injected into the disposal well.

Samples from the Radioactive Waste Management Complex (RWMC) at the INEEL were also analyzed for this project. Waste buried in drums in shallow pits at the RWMC contained significant amounts of chlorinated solvents and lubricating oils. Leaks in the drums have resulted in a plume of vapor-phase contaminants in the unsaturated zone. The primary goal of our work was to determine the extent of natural degradation of contaminants in the unsaturated zone. Over a two-year period, the concentrations and isotopic ratios of CO_2 in gas samples taken from monitoring wells at the site were measured. The concentrations of CO_2 in shallow gas samples (10-25 m) from the vicinity of the disposal pits were significantly elevated relative to the concentrations of CO_2 in background wells. Further, the $d^{13}C$ values of the CO_2 from the contaminated area were lower than the CO_2 from the background wells, suggesting that the CO_2 was derived from the organic contaminants. In addition,

the ^{14}C content of several of the high-CO_2 samples was very low; indicating that they were produced from chemicals derived from fossil fuels.

In the final year of the project, work was focused on obtaining isotopic data for groundwater samples from the Hanford site. As a result of production of fuel for nuclear weapons during the cold war period, significant amounts of radionuclides were released to the environment at Hanford. The goal of our work was to identify pathways and mechanisms of infiltration of the wastewater through the unsaturated zone to the groundwater. Preliminary results indicate that the strontium isotope ratio of the groundwater is a very effective indicator of the proportion of wastewater dumped at the surface that has mixed with the groundwater. In addition, other isotopic measurements are indicative of other processes such as evaporation, degradation of organic matter and interaction with carbonate minerals in the subsurface. All of these isotopic signals hold great promise for identifying specific waste streams and tracking their infiltration to groundwater.

The results of these studies clearly demonstrate how isotopic measurements can be used to help answer questions of critical importance for environmental management. Our primary findings are:

1. ***Natural (or intrinsic) biodegradation of chlorinated hydrocarbons can be documented by measurements of natural isotopic tracers.***
2. ***Engineered biodegradation can be verified by measurements of natural isotopic tracers.***
3. ***Natural isotopic tracers can be used for basic characterization of groundwater systems in lieu of injection experiments.***

Further, these studies have produced important field data about basic scientific processes such as the infiltration of water through the unsaturated zone and the potential for subsurface biologic activity in arid environments. At both the INEEL and Hanford, the scientific collaborations that have been developed between the researchers from the Berkeley Lab and the investigators from the sites have led to proposals of additional studies using the principles developed through this project.

Information Access

Conrad, M.E., D.J. DePaolo, D.L. Song, and E. Neher, 1999, Isotopic evidence for groundwater flow and biodegradation of organic solvents at the Test Area North site, Idaho National Engineering and Environmental Laboratory: In *Ninth Annual V.M. Goldschmidt Conference*, pp. 58-59, LPI Contribution No. 971, Lunar and Planetary Institute, Houston.

Song, D.L., L. Alvarez-Cohen, M.E. Conrad, and K. Sorenson, 1999, Monitoring of enhanced in-situ bioremediation of trichloroethylene using stable carbon isotopes: *Program and Abstracts for the 4th International Symposium on Subsurface Microbiology*, Vail, Colorado.

Conrad, M.E., D.J. DePaolo, B.M. Kennedy, and E.C. Miller, 1997, Carbon isotope evidence for degradation of mixed contaminants in the vadose zone: *Geol. Soc. Am., Abst. with Prog. 26, no. 6*, A186.

Evaluation of Isotopic Diagnostics for Subsurface Characterization and Monitoring: Field Experiments at the TAN and RWMC (SDA) Sites, INEEL

Project ID: 55351

Dr. Donald J. DePaolo, Lawrence Berkeley National Laboratory

Research Objectives

The research will explore and refine the use of isotopic ratio measurements on aquifer groundwaters and vadose zone gas for improving remediation strategies and increasing the efficiency of ongoing remediation activities at the TAN and RWMC (SDA) sites at Idaho National Engineering and Environmental Laboratory. The measurements to be made are ?^{13}C, ?^{14}C, ?^{18}O, ?D, ^{87}Sr/^{86}Sr, and ^{37}Cl/^{35}Cl isotopic ratios, and the abundances and isotopic compositions of the noble gases He, Ne, Ar and Xe.

The isotopic ratios are used in conjunction with water and gas chemistry to determine: (1) the extent and nature of chemical reactions in the TAN plume and their role in retardation of radioactive isotopes ^{90}Sr and ^{137}Cs and the attenuation of dissolved chlorinated hydrocarbons; (2) predict the chemical effects of proposed remediation techniques (bioremediation, oxidation, and grout barrier installation) on transport in the plume; (3) the extent of natural degradation of chlorinated hydrocarbons in the TAN plume, and the transport of gases through the vadose zone from the plume; (4) the extent of natural remediation and in situ transformations of volatile organic compounds at the SDA site; (5) the extent of recirculation of surface air during VVE activities, and how this changes with season and barometric conditions. The data collected will provide a unique characterization of transport processes in the aquifer and the vadose zone, and an evaluation of the benefits of isotopic approaches in support of remediation activities at two representative sites.

The proposed studies are to be carried out in cooperation with the LITCO-supervised characterization and remediation activities at the TAN and RWMC (SDA) sites at INEEL. Most of the sampling necessary for the study is covered by normal sampling schedules; additional sampling can be done in existing wells or with soil gas sampling equipment.

Molecular-Level Processes Governing the Interaction of Contaminants with Iron and Manganese Oxides Project

Project ID: 54635

S.A. Chambers, Pacific Northwest National Laboratory

G.E. Brown, Jr., Stanford University of Geological and Environmental Sciences and Stanford Synchrotron Radiation Laboratory

Research Objective

The central tenet of this program is that *a fundamental understanding of specific mineral surface-site reactivities will substantially improve reactive transport models of contaminants in geologic systems, and will allow more effective remediation schemes to be devised.*

Research Progress and Implications

To this end, we carried out a program of research that focuses on the fundamental mechanisms of redox chemistry of contaminants on mineral surfaces. As much of this chemistry in sediments involves the Fe(III)/Fe(II) couples, we focussed on mineral phases containing these species. Our approach was to conduct carefully controlled experiments on model, single-crystal Fe oxide mineral surfaces grown by molecular beam epitaxy, natural Fe oxide single crystals, and synthetic mineral powders. We used the results from the model surfaces, which were very well defined in terms of surface composition, structure, and defect densities, to understand the results obtained on more complex mineral specimens. We used a variety of experimental probes, along with molecular modeling theory, to determine clean mineral surface structure, details of the chemisorption and decomposition of water, and the interface structure and redox chemistry of important contaminants such as CrO_4^{-2} on these surfaces.

This report summarizes work completed during the entire three years.

•*Studies on Single Crystal Iron Oxide Surfaces*

We have studied the interaction of aqueous chromate (CrO_4^{-2}) with the iron oxides hematite (α-Fe_2O_3) and magnetite (Fe_3O_4). Model surfaces of hematite and magnetite were grown by oxygen-plasma-assisted molecular beam epitaxy on single crystal substrates of α-Al_2O_3 and MgO, respectively. Natural specimens were also used for water and chromate chemistry experiments. Clean surface composition, geometric structure and morphology were investigated experimentally using a combination of x-ray photoelectron spectroscopy and diffraction, and scanning tunneling microscopy. Theoretical surface structure predictions were also made using molecular dynamics (MD) simulations. It was found that a simple surface autocompensation model is adequate to predict the stable terminations(s) of these surfaces. The interlayer relaxations were experimentally determined and found to compare favorably with MD simulations for hematite, but not magnetite. These surfaces were then exposed to the pure solvent (H_2O) in a controlled fashion from the vapor phase to investigate surface hydroxylation. Using x-ray photoelectron spectroscopy, it was found that both surfaces exhibit a threshold pressure for hydroxylation of ~10^{-3} - 10^{-4} torr which appears to be dictated by thermodynamic driving forces, rather than kinetics. The kinetics of reduction of Cr(VI) in CrO_4^{-2} to Cr(III), and the structure of adsorbed Cr(III) on surfaces initially containing Fe(II), were then determined using x-ray photoemission, x-ray absoprtion spectroscopy, and extended x-ray absorption fine structure. The reduction kinetics were found to be highly pH dependent, with the fastest rates occurring at pH values below the point of zero charge of magnetite (i.e. those pH values for which

the surface is positively charged). At the highest rate, the surface redox reaction is ~90% complete within 5 minutes, leaving behind a thin (15±5Å) layer of mixed, insulating Cr oxyhydroxide that shuts down the electron transfer process. The reduction product, Cr(III), is bound as an inner-sphere (i.e. no mediating waters) edge-sharing, bidentate complex on the oxidized surface. The CrO_4^{-2} reduction kinetics on magnetite single crystals were found to be almost identical to those measured earlier on "zero-valent iron" powders. This fact strongly suggests that it is the magnetite native oxide on the surface of such particles that interacts chemically with sorbed CrO_4^{-2} rather than Fe(0). In addition, the fact that the process ceases after just a few minutes, with the formation of an ultrathin, insulating oxyhydroxide layer, establishes that the latter quenches charge transfer above a critical thickness of ~15Å. Thus, deployment of such a remediation process will be "surface limited" and high surface area materials will be required to reduce a significant amount of CrO_4^{-2}.

•*Studies on Hematite Powder*

Powdered hematites present several crystalline faces for surface reactions and thus represent a system that is intermediate in complexity between the single-crystal surfaces described above and the heterogeneous mixture of surfaces found in soils and sediments. We conducted several experiments with hematite powder to understand the thermodynamics and kinetics of CrO_4^{-2} sorption, with particular emphasis placed on competitive sorption by chromate, phosphate and sulfate oxyanions by laser photoacoustic spectroscopy (LPAS). Sorption of CrO_4^{-2} and phosphate species to hematite is dominated by divalent anions even at low pHs where monovalent anions predominate in solution. As a consequence, aqueous speciation (i.e. the fraction of the total species in solution available in the form of a divalent anion) is a more important determinant of the relative amount of CrO_4^{-2} or phosphate sorbed than the intrinsic selectivity of the anions for the surface. In mixed-anion systems typical of groundwater, significantly different sorption affinities may be observed than predicted solely on the basis of relative single-anion sorption constants.

An important outcome of this work is the development of a powerful new tool with which competitive adsorption of anions on minerals in suspension can be investigated in real time. We have demonstrated that nontoxic anions present in the subsurface environment, such as phosphate, may compete with toxic anions, such as CrO_4^{-2}, for sorption sites on redox-active minerals to an extent that is highly pH dependent. Significantly, LPAS can be used for studies of pure mineral phases, such as hematite in the present experiments, as well as for multi-component soil mixtures. Thus, controlled and "real-world" experiments can be carried out to determine the extent to which competing nontoxic anions can prevent adsorption and reduction of toxic anions by minerals or redox-active remediation agents, such as zero-valent iron.

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

Project ID: 70088

B. Deng, New Mexico Institute of Mining and Technology

E.C. Thornton, Pacific Northwest National Laboratory
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Research Objectives

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

The objective of this project is to seek basic scientific understandings concerning the kinetics and mechanisms of interactions among H_2S, the metal contaminants, and soil components. Within a three-year period of the project, the following specific research tasks will be accomplished: (A) Evaluation of the potential catalytic effect of mineral surfaces on the rate of Cr(VI) reduction by H_2S and the rate of H_2S oxidation by air, (B) Identification of the reactions of soil minerals with H_2S and determination of associated reaction rates, (C) Evaluation of the role of soil water chemistry on the reduction of Cr(VI) by H_2S, (D) Assessment of the reductive buffering capacity of H_2S-reduced soil and the potential for emplacement of long-term vadose zone reactive barriers, and (E) Evaluation of the potential for immobilization of Tc and U in the vadose zone by reduction and an assessment of the potential for remobilization by subsequent reoxidation. A substantial amount of work will be accomplished on Tasks A-D during FY2000. Task E will be completed in the FY2001-2002.

Research Progress and Implications

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

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

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

Planned activities

Substantial progress is being made in FY2000 that has greatly increased our understanding of reaction processes in the Cr(VI)-H_2S-O_2-Soil System. In the FY2000-2001, we plan to continue with the Tasks A-D in order to obtain information needed to support reactive transport modeling activities and design of ISGR field treatment systems. (1) A substantial number of column tests will be performed on Hanford soil samples to define reaction stoichiometries and kinetics in the Cr(VI)-H_2S-O_2-Soil System. This work includes performing tests over a range of gas flow conditions in order to obtain information regarding the rates of competing or coupled reactions. Treated soils are also being characterized for iron and sulfur products, and mass balance considerations will be employed to define the specific H_2S/soil reactions involved. Long-term oxidation tests (6-month duration) will also be performed on H_2S-treated soil samples to verify that the reduced chromium will not be reoxidized. (2) Solid-gas phase interactions between synthesized iron oxides (e.g., ferrihydrite and hematite) and H_2S will be examined through column studies. The amount of H_2S consumed will be determined. The reaction products will be analyzed by Mössbauer, X-ray photoelectron, and far-infrared spectroscopies. This will serve to better define H_2S interaction processes in soils. (3) Experiments on aqueous phase Cr(VI) reduction by sulfide under various conditions will be completed and the reaction mechanism will be explored. In particular, the effect of oxygen will be tested. (4) Potential catalysis of mineral surface on Cr(VI) reduction by sulfide will be examined using pure Fe-, Mn-, Al-, and Si- oxides as representative surfaces. Adsorption of both Cr(VI) and sulfide will be properly evaluated in order to understand the catalytic processes. (5) Interactions between pure chromate compounds (e.g., K_2CrO_4, Na_2CrO_4, $BaCrO_4$, $CaCrO_4$) and H_2S gas will be tested. Reaction products will be analyzed by X-ray diffraction, SEM, and TEM with parallel electron energy-loss spectroscopy (PEELS). In addition, testing activities will be extended in FY 2001 to include Tc and in FY 2002 to include U, thus potentially increasing the capabilities of the ISGR remediation approach.

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

Cavitational Hydrothermal Oxidation: A New Remediation Process

Project ID: 55211

Dr. Kenneth S. Suslick, University of Illinois at Urbana-Champaign

Research Objectives

This research will explore the emerging science of sonochemistry and its technological applications for organic waste remediation, particularly for water and soil purification. Ultrasound can induce unusual high-energy chemistry through the process of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation can occur both in clouds of collapsing bubbles (multi-bubble cavitation, MBC) or with high symmetry for isolated bubble (single-bubble cavitation, SBC). Multi-bubble cavitational collapse produces localized, transient hot spots with intense local heating (~5000K), high pressures (~2000 atm), and short lifetimes (sub-microsecond) in an otherwise cold liquid. From hydrodynamic modeling of this cavitational collapse, we can estimate that both the heating and cooling rates are in excess of 1010 K/sec, which is faster than splat-cooling of molten metals onto liquid He cooled surfaces! Acoustic cavitation is a unique means of creating high energy chemistry, easily and inexpensively. Aqueous sonochemistry produces, on a microscopic scale, supercritical water conditions with a vengeance! The applications of cavitation to remediation of toxic organics, however, has only begun to be explored in a convincing fashion.

In this regime of temperature and pressure, the sonochemistry of water is an extreme limiting case of supercritical phenomena and is closely related to hydrothermal oxidation (HTO). For example, the ultrasonic irradiation of water produces a variety of extraordinarily reactive species (including OH*, H*, and HO2) capable of decomposing essentially all organic compounds. Furthermore, the temperatures reached in the cavitation hot spots are sufficient to pyrolyze all volatile organic compounds.

Our overall goal in this research is to develop our understanding of the reactions of organic compounds in the presence of high intensity ultrasound. Our specific objectives in this proposed work fall into four areas: 1) investigation of the local conditions formed during cavitation in water; 2) mechanistic examination of the effects of cavitation on polycyclic aromatic hydrocarbons, nitroaromatics, and halocarbons; 3) determination of degradation yields as a function of experimental configurations of aromatics and halocarbons as toxic impurities in water, and 4) design and testing of large scale flow processing systems useful for remediation of contaminated water. In all cases, we will continue our special emphasis on the mechanistic origins of sonochemistry, in relationship to its applications to environmental challenges. Information gained should lead to effective protocols and equipment designs for large scale treatment of contaminated water and soil slurries

The Pimentel Report ("Opportunities in Chemistry", National Research Council) in their first recommendation noted five research frontiers which should receive priority: one of these is "Chemical Behavior Under Extreme Conditions". The committee stated our thesis perfectly: "We propose an initiative to explore chemical reactions under conditions far removed from normal ambient conditions. Chemical behaviors under extreme pressures, extreme temperatures, ... provide critical tests of our basic understandings of chemical reactions and new routes toward discovery of new materials and new devices" (p. 12). Chemistry, after all, is the interaction of energy and matter, and the energy source often determines chemical reactivity. One way of representing these interactions is to visualize a three-dimensional space with axes of pressure vs. energy vs. time of interaction. Sonochemistry provides a unique access to regions of this reactivity-space and represents a distinct class of interaction of energy and matter. Ultrasound induces this unusual high-energy chemistry through the process of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. Acoustic

cavitation is the underlying phenomenon which is responsible for sonochemistry and sonoluminescence.

In spite of early work in the area of sonochemistry, interest within the chemical community remained exceedingly modest until the 1980's. With the advent of inexpensive and reliable sources of ultrasound, however, sonochemistry has undergone a dramatic renaissance. As our understanding of the nature of the chemical effects of ultrasound has grown, so too has the impact of sonochemistry on the chemical community. We have discovered a variety of chemical consequences of these phenomena, including dramatic improvements in both catalytic and stoichiometric reactions of organometallics, metal surfaces, and semiconductor powders. We have developed unique sonochemical syntheses of novel amorphous and nanophase materials unavailable by other techniques. And, we have found important biomedical applications involving sonochemical production of proteinaceous microspheres. Thus the scientific impact of sonochemistry has promise in a wide range of the physical sciences.

Sonochemistry also has substantial strategic research significance to our industrial economy. Ultrasound has already major industrial applications, and the U.S. completely dominates the world market in the production of ultrasonic equipment. Commercial ultrasound equipment for large scale liquid processing is available off-the-shelf at quite modest costs. It is extremely important in solids processing, including cutting, welding, cleaning and precipitation. Ultrasonic cleaning, for example, now dominates both general purpose industrial and microelectronics applications, due to increasing restrictions on the use of halocarbon and other organic solvents. Ultrasound is an already established technology for industrial emulsification, solvent degassing, solid dispersion, cell disruption, and sol formation (e.g., fume scrubbers).

Biofiltration of Volatile Pollutants: Fundamental Mechanisms for Improved Design, Long-term Operation, Prediction, and Implementation

Project ID: 55013

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K. Thomas Klasson, Oak Ridge National Laboratory
John W. Barton, Oak Ridge National Laboratory

Research Objective

Biofiltration systems can be used for treatment of volatile organic compounds (VOCs); however, the systems are poorly understood and are currently operated as "black boxes". Common operational problems associated with biofilters include fouling, deactivation, and overgrowth, all of which make them ineffective for continuous, long-term use. The objective of this investigation is to develop generic methods for long-term stable operation, in particular by using selective limitation of supplemental nutrients while maintaining high activity. As part of this effort, we will provide deeper fundamental understanding of the important biological and transport mechanisms in biodestruction of sparingly soluble VOCs and extend this approach and mathematical models to additional systems of high priority EM relevance - direct degradation and cometabolic degradation of priority pollutants such as BTEX and chlorinated organics.

Research Progress and Implications

This report summarizes progress during the third year of a 3-year project. Major results are enumerated and discussed below.

1. A manuscript detailing how to control biofilm overgrowth, while sustaining high degradation rates, in operating trickle-bed bioreactors has been submitted for publication. Optimal results were achieved by limiting either ammonium, sulfate, or calcium in the liquid recycle stream. Each of these allowed for decoupling of growth and degradation such that long-term operation was possible. Other nutrients examined, including chlorine, magnesium, phosphate, and nitrate, were not effective and resulted in either continued growth or minimal degradation rates. These results are important for enabling longer term operation of traditional biofiltration units.
2. Further development of a comprehensive two-dimensional predictive model to elucidate mass transfer and kinetic limitations in these systems was made. This model can be extended to a variety of columnar biofiltration systems by changing appropriate parameters. This user-friendly model/program can be installed and run independently on any IBM-compatible personal computer using Microsoft Windows 95/98.
3. Fundamental measurements of Henry's law coefficients for a variety of sparingly soluble alkanes in biomass were made; results indicated that these compounds have substantially higher solubilities in aqueous biomass than in pure water (see Figure). Since predictive calculations for bioprocesses are strongly affected by the magnitude of the Henry's law parameters, new correlations/measurements are needed to compensate for this effect. These data could have a significant impact on current models being used for subsurface transport and clean up strategies. A proposal for follow-on/extension funding in this specific area is being submitted.
4. A manuscript detailing the effects of biomass on Henry's law constants has been accepted for publication in Biotechnology and Bioengineering.

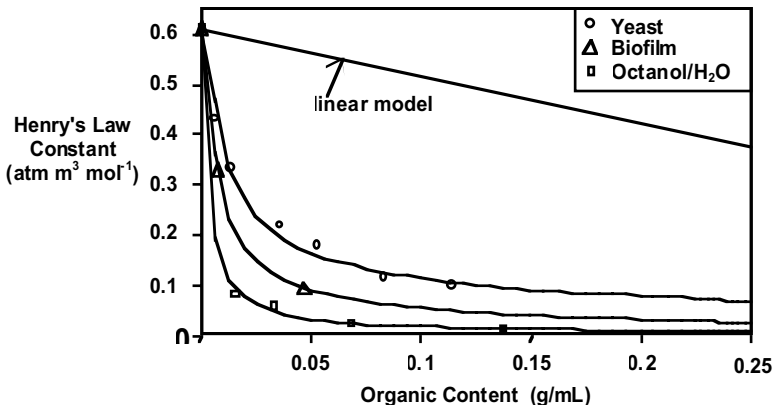

Figure. Unpublished preliminary data for propane which show deviation from ideal models of partitioning between biomass and gas phases (as would be likely in vadose zones and surface impoundments). Data were collected for yeast (circles) and bacteria (triangles) over a variety of organic densities and compared to two 'ideal models' for octanol/water partitioning (squares and straight line). In both cases, actual partitioning measurements deviated significantly from idealized models for pure water/octanol mixtures.

5. Isolation of a microorganism capable of degrading a variety of VOC's and chloroorganics was completed. The organism was identified as a slow-growing, aerobic, gram-positive rod. By identifying the strain responsible, quick seeding of the biofilters is much simpler than using a mixed consortium. DNA typing is pending.
6. Kinetic factors associated with growth of the above-mentioned organism were quantified, including specific growth rate and saturation constant. These factors are useful in describing uptake and cell division in mathematical models.
7. Degradation of BTEX compounds in column biofiltration units was initiated this year.
8. Experiments designed to test alternative packing and 'seeding' strategies were initiated this year. These experiments examine new matrices for rapid bacterial adhesion/start-up and long-term stability.

Planned Activities

1. Extension of the mathematical model to other biofiltration systems
2. Publication of the model/Windows 95 program code on the World Wide Web
3. Measurement of solubilities and Henry's law constants of critical contaminants (TCE, BTEX, etc.) in biomass.

Information Access

A number of peer-reviewed publications have been submitted and/or accepted based on some of the results from this work. Several presentations at national scientific conferences have been given or are currently scheduled to be delivered during this calendar year. A complete list of submitted papers and presentations may be found below. More information is available at http://www.etde.org/html/em52/55013.html

Peer-reviewed publications during past year

Davison, B.H., J.W. Barton, K.T. Klasson, A. F. Francisco. "Influence of Biomass on Alkane Solubilities" In press.

Francisco, A.F., J.W. Barton, K.T. Klasson, and B.H. Davison, "Nutrient Limitation Effects on a Microbial Consortium in Trickle-Bed Bioreactors," submitted for publication.

Klasson, K. T., J. W. Barton, and B. H. Davison. Performance of a Propane-degrading Bacterium. Proceedings of the 92nd Annual Meeting of the Air and Waste Management Association, June 1999.

Barton, J. W., B. H. Davison, K. T. Klasson, and C. C. Gable III. Estimation of Mass Transfer and Kinetics in Operating Trickle-Bed Bioreactors for Removal of VOCs. *Environ. Prog*. 18:1-5, 1999.

Barton, J. W., X. S. Zhang, B. H. Davison, and K. T. Klasson. Predictive Mathematical Modeling of Trickling Bed Biofilters. Proceedings of the 1998 USC-TRG Conference on Biofiltration, October 22-23, Los Angeles, CA.

Barton, J. W., X. S. Zhang, K. T. Klasson, and B. H. Davison, Predictive Mathematical Modeling of Trickling Bed Biofilters for Elucidating Mass Transfer and Kinetic Effects, Proceedings of the 91st Annual Meeting of the Air and Waste Management Association, San Diego, CA, June 1998. Paper 98-WAA.13P.

Klasson, K. T., B. H. Davison, J W. Barton and J. E. Jacobs, Removal of Chlorinated and Nonchlorinated Alkanes in a Trickling Bed Biofilter, Proceedings of the 91st Annual Meeting of the Air and Waste Management Association, San Diego, CA, June 1998. Paper 98-WAA.06P.

Barton, J. W., S. Hartz, K. T. Klasson, and B. H. Davison, Microbial Removal of Alkanes from Dilute Gaseous Waste Streams: Mathematical Modeling of Advanced Bioreactor Systems," *J. Chem. Technol. Biotechnol.* **72**:93-98 (1998).

Use of Sonication for In-Well Softening of Semivolatile Organic Compounds

Project ID: 55374

Robert W. Peters, Argonne National Laboratory

Onder Ayyildiz, Illinois Institute of Technology
Michael R. Hoffmann, California Institute of Technology
Steven Gorelick, Stanford University

Research Objective

This project investigates the *in-situ* removal/destruction of semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) from groundwater using in-well acoustic cavitation (sonication), in-well vapor stripping, and biodegradation. The project has the primary objectives of developing this integrated system for efficient and economical removal and degradation of SVOCs and VOCs from groundwater. The project has as its goal the partial degradation (softening) of the more recalcitrant organic compounds in order to convert them into compounds that are more amenable to both vapor stripping and biological degradation. By performing the integrated sonication/vapor stripping in-well, the treated groundwater can be reinjected and percolated through the subsurface, thereby enhancing biodegradation by generating organics that are more easily biodegraded.

Research Progress and Implications

This report summarizes work from over 3+ years of research on this topic. Argonne National Laboratory is developing a new integrated technology combining in-well sonication/in-well vapor stripping, and *in-situ* biodegradation for removal of VOCs and SVOCs from solution. This technology has recently been described in the technical literature [***HazTech News***, 2000]. Bench-scale batch and continuous flow experiments have been performed involving sonication alone, vapor stripping alone, and combined sonication/vapor stripping. Organic contaminants studied include: carbon tetrachloride (CCl_4), trichloroethylene (TCE), trichloroethane (TCA), and tetrachloroethylene (PCE). Initial organic concentrations range from ~1 to ~100 mg/L.

Figure 1 shows the results from batch treatment of groundwater containing ~50 mg/L of the chlorinated organic compounds, using both sonication alone and sonication+vapor stripping for a low power intensity of 12.3 W/cm^2. After 10 minutes treatment time, removal of the chlorinated organic contaminants by sonication alone ranges from ~16% to~26%, whereas the removal in the combined sonication/vapor stripping (air injection rate of 500-mL/min) system exceed 96% after 10 minutes treatment; after 6 minutes treatment time, removals exceeded 87% in the combined system. The removal of chlorinated organics by these techniques follows first-order kinetics. The rate constants are typically on the order of 0.03-0.05 min^{-1} using sonication alone; ~0.2 min^{-1} using vapor stripping alone, and 0.45-0.65 min^{-1} for the combined system; increasing the air injection rate in the combined system from 500-mL/min to 1000-mL/min increased the rate constant to 0.50 to 0.90 min^{-1}. Figure 2 shows the residual TCE concentration following application of sonication alone and sonication+vapor stripping for continuous flow conditions; for reactor residence times ranging from 5 to 10 minutes, removals of CCl_4 and TCA were 74% to 88% and 72% to 97%, respectively, for a one-pass system. Sonication alone or vapor stripping alone results in removals ranging from ~20% to ~50%; however, combining sonication with vapor stripping enhances removal of CCl_4, TCE, TCA, and PCE as compared to removal by either system alone (sonication or vapor stripping) by nearly an order of magnitude, and results in synergistic behavior enhancing removal efficiency. The combination of

sonication with vapor stripping results in much better mixing, creation of much finer bubbles, thereby enhancing mass transfer from the liquid phase to gaseous phase, and enhancing the destruction of the chlorinated organic compounds during the microbubble implosions. Laboratory results are presented in this poster for the removal of CCl_4, TCE, TCA, and PCE from groundwater using acoustic cavitation and/or vapor stripping treatment techniques operated in a continuous flow manner. Analysis of the degradation products indicates that C_2Cl_4 and C_2Cl_6 are the primary intermediates formed from sonication of waters containing CCl_4; a maximum concentration of ~0.04% of CCl_4 appears as C_2Cl_4, and <0.0125% appears as C_2Cl_6, respectively. These compounds are readily degraded during aqueous-phase sonication.

As we move to higher ultrasonic frequencies and greater applied power densities, plus incorporation of multiple frequencies and improved focusing and directionalizing of acoustic waves, the system performance is expected to be even better in the pilot-scale and field demonstration phases as compared to the laboratory data reported here. In moving the technology towards pilot-scale and field-demonstration activities, an industrial partner (Furness-Newburge, Inc.) has been added.

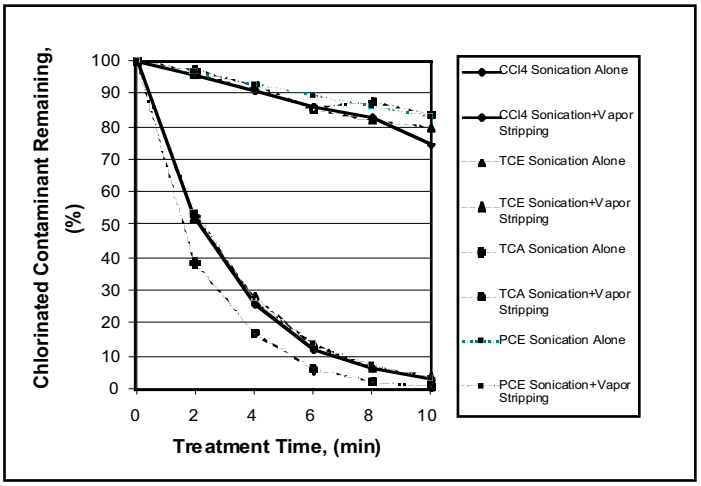

Fig. 1. Residual chlorinated organic compound remaining after batch sonication and sonication+vapor stripping treatment.

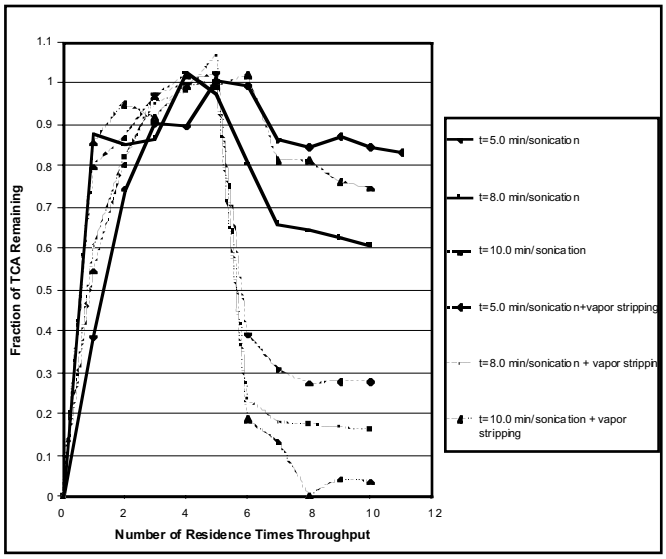

Fig. 2. Residual chlorinated organic compound remaining after continuous sonication and sonication+vapor stripping treatment.

Planned Activities

Work currently in progress involves completion of the continuous flow sonication/vapor stripping experiments involving TCE and PCE. Work is planned for investigating the removal of multiple chlorinated organic contaminants (rather than existing as single contaminants) to investigate whether the contaminants interact either in a synergistic or antagonistic fashion. Work is also underway investigating the use of this integrated technology to treat groundwaters contaminated with petroleum hydrocarbons. In follow-on funding currently being pursued, the treatment system will be scaled up to conduct a pilot-scale demonstration (capable of treating up to ~200 gallons) and perform a field demonstration at a selected DOE facility.

Other Access to Information

- Peters, R.W., M.L. Wilkey, J.C. Furness, and O. Ayyildiz, (2000). "Development of the Integrated In-Well Sonication/In-Well Vapor Stripping System to Treat Chlorinated Solvent-Contaminated Groundwater", Paper presented in the Topical Conference on "Environmental Remediation in the 21st Century: Integrated Systems Technologies", Spring National AIChE Meeting, Atlanta, GA, (March 5-9).
- Peters, R.W., M. Wilkey, O. Ayyildiz, M. Quinn, L. Pierce, M. Hoffmann, and S. Gorelick, (1998). "Use of Sonication for In-Well Softening of Semivolatile Organic Compounds", *Proc. DOE Environmental Management Science Program Workshop*, Chicago, IL, (July 27-30).

Nuclear Magnetic Resonance Imaging of Water Content in the Subsurface

Project ID: 54857

Dr. Jan M.H. Hendrickx, New Mexico Institute of Mining and Technology

Dr. T. (Mike) Yao, New Mexico Institute of Mining and Technology
Anne Kearns, New Mexico Institute of Mining and Technology

Executive Summary

This report contains the experimental, theoretical and numerical studies performed under Department of Energy (DOE) Agreement Number DE-FG07-96ER14732 entitled "Surface Nuclear Magnetic Resonance for Imaging Subsurface Water."

DOE and Department of Defense (DOD) complexes and test ranges are situated in widely varying climatic conditions from the desert southwest to the humid east. The mission of the Office of Environmental Restoration and Waste Management (EM) is to clean up the inventory of inactive DOE sites and facilities, and the goal of the EM Office of Technology Development (OTD) is to deliver technologies to make environmental restoration more efficient and cost effective. In the western United States, where a number of DOE facilities are located, the water table can occur several hundred feet below the surface. The zone between surface and water table is called the vadose zone or unsaturated zone. A characteristic of that zone is that mobility of water and contaminants is greatly reduced compared to rate of movement in the saturated zone. A thick vadose zone lowers the risk and, at least, increases the time before contaminants enter drinking water supplies. The assessment of risk is often performed by modeling of groundwater flow and contaminant migration by analytical methods or unsaturated flow models (e.g. Hendrickx *et al* 1991). Necessary inputs for these models are the hydraulic properties of the different geological formations (e.g. Hendrickx 1990) and the water content distribution in the vadose zone (Freeze and Cherry 1979). Accurate risk assessments for groundwater contamination cannot be conducted without actual measurements of the water content distribution in the vadose zone. To date, very few techniques have been developed to provide such information at an acceptable speed and cost. Because soil water contents exhibit a large spatial and temporal variability, the costs of conventional measurement techniques, such as gravimetric sampling, gypsum blocks, and neutron probes, are high. Only non-intrusive tests with a cost factor much lower than that of an intrusive test will offer acceptable alternatives. Therefore, a definite need exists for a non-intrusive water content measurement method.

The surface nuclear magnetic resonance (NMR) technique applied to imaging of groundwater was first developed by Russian scientists from the Institute of Chemical and Combustion in Novosibirsk, Russia. Over the last two decades they have published a series of papers and reports describing the theory of the method, along with experimental measurements from the surface to a depth of about 100 m. Preliminary evaluation of the concepts and results merited further investigations, particularly because of the critical technical need for cost-effective water content measurements in environmental restoration.

Research Progress and Implications

The work under this contract proceeded along two parallel directions:

- Experimental NMR measurements at sites in Colorado and New Mexico with control on geologic and hydrogeologic conditions. The equipment used for the measurements was the

NUMIS equipment manufactured by IRIS Instruments of fiance. This equipment follows the design of the original equipment of the Russian scientists.

- Generalization of the NMR theory to correctly model the NMR response from conductive ground, along with numerical implementation of the corrected theory to assess significance of the theoretical corrections and to understand properties of the inverse problem.

Concurrent with our investigations of surface NMR imaging of water content in the subsurface, active development was ongoing in oil exploration and oil service companies on NMR logging in boreholes, and by laboratory measurements on samples to better understand the NMR response of water in soils and rocks. NMR logging is rapidly becoming an important tool in reservoir engineering because in principle information about permeability can be derived.

The results from the experimental measurements performed under this contract show that the ability to record reliable data and infer water content distributions from the data is site specific. Proper inference of water content requires knowledge of the geolectric section, which must be obtained from a separate measurement and is often known only with limited accuracy. Present equipment limitations sometimes preclude obtaining reliable measurements of water content in several soil and rock types, such as soils and rocks with magnetite (ferromagnetic mineral) and fine grained soils. At sites where reliable measurements were recorded, the tool shows the power of the technology in that constraints on *both* water content and permeability may be obtained. The published literature describes case histories at highly selective sites and does not adequately address several of the technique's limitations. Under this contract, experimental measurements were made at sites with widely varying hydrogeologic conditions, so that the range of applications and limitations could be evaluated. Major advances were made in development of the theory and the computational algorithms and programs to derive water content from surface NMR measurements.

Information Access

Freeze, R.A., and Cherry, J.A., 1979, *Groundwwater* (Prentice Hall).

Hendrickx, J.M.H., 1990, *Determination of hydraulic soil properties,* in *Process studies of hillslope hydrology,* Chapter 3, pp. 42-93, M.G. Anderson and T.P. Burt, eds. (John Wiley and Sons).

Hendrickx, J.M.H., Khan, S., Bannink, M.H., Birch, D., and Kidd, C., 1991, *Numerical analysis of groundwater recharge through stony soils using limited data,* J. of Hydrology **127**, 173-192.

Investigation of Pore Scale Processes That Affect Soil Vapor Extraction

Project ID: 70045

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Charles J. Werth, University of Illinois at Urbana-Champaign
Andrew G. Webb, University of Illinois at Urbana-Champaign

Research Objective

Dense nonaqueous phase liquid (DNAPL) contamination in the vadose zone is a significant problem at Department of Energy sites. Soil vapor extraction (SVE) is commonly used to remediate DNAPLs from the vadose zone. In most cases, a period of high recovery has been followed by a sustained period of low recovery. This behavior has been attributed to multiple processes including slow interphase mass transfer, retarded vapor phase transport, and diffusion from unswept zones of low permeability.

Prior attempts to uncouple and quantify these processes have relied on column experiments, where the effluent concentration was monitored under different conditions in an effort to quantify the contributions from a single process. In real porous media these processes occur simultaneously and are inter-related. Further, the contribution from each of these processes varies at the pore scale and with time.

This research aims to determine the pore-scale processes that limit the removal of DNAPL components in heterogeneous porous media during SVE. The specific objectives are to: 1) determine the effect of unswept zones on DNAPL removal during SVE, 2) determine the effect of retarded vapor phase transport on DNAPL removal during SVE, and 3) determine the effect of interphase mass transfer on DNAPL removal during SVE, all as a function of changing moisture and DNAPL content. To fulfill these objectives we propose to use magnetic resonance imaging (MRI) to observe and quantify the location and size of individual pores containing DNAPL, water, and vapor in flow through columns filled with model and natural sediments. Imaging results will be used in conjunction with modeling techniques to develop spatially and temporally dependent constitutive relations that describe the transient distribution of phases inside a column experiment. These constitutive relations will be incorporated into a site-scale transport model to evaluate how the different processes affect SVE performance in practical applications. This will allow decision makers to better assess the risk associated with vadose zone contamination and the effectiveness of SVE at hazardous waste sites.

Research Progress and Implications

The project commenced on September 15, 1999. In the brief time since the project began, we have focused our efforts on initial planning and organization. We have one part-time graduate research assistant and one undergraduate research assistant that just began working on the project in January of 2000; and we are actively searching for one post-doctoral associate and another graduate assistant.

The part-time graduate research assistant, a Ph.D. student in electrical engineering, is developing a computer algorithm that will be used to interpret the images from our flow-through column experiments. As described in our project proposal, magnetic resonance imaging will be used to take 3-D "snapshots" of the distribution of water, NAPL, and air in columns purged with vapor at selected time intervals. Each snapshot (or image) will contain up to 256^3 voxels (a voxel is a 3-D pixel); and each voxel will have a single gray scale value that is a function of the phase (or phases) in the voxel. For example, voxels that contain water will be light, voxels that contain NAPL will be light gray, and

voxels that contain air will be black. The computer algorithm under development presently uses thresholding and nearest neighbor arguments to count the number of discrete NAPL blobs (i.e. the number of clusters with a common gray scale value) in an image. Further development will allow us to quantify parameters such as the surface area of each NAPL blob, the surface area distribution of all NAPL blobs, the number of water filled pores, and the surface area distribution of water filled pores.

The undergraduate research assistant, a student in civil and environmental engineering, is conducting sorption/desorption experiments on dry solids. As described in our project proposal, we will measure sorption and desorption rates at different relative humidities. As a first step toward completing this task, the undergraduate research assistant has packed columns with dry solids and is preparing to contaminate them.

Planned Activities

The part-time graduate research assistant will complete development of the algorithm that will be used to analyze imaging results by June of 2000. This student will apply the algorithm to imaging results that we are currently collecting on another project that is examining NAPL dissolution under water saturated conditions.

The undergraduate student will complete sorption and desorption experiments on dry solids by June of 2000. A part-time graduate student will be hired in the Fall of 2000 that will start sorption and desorption experiments at different relative humidities. These experiments will take approximately 1 year to complete.

A post-doctoral research associate will be hired in the Summer or Fall of 2000 to conduct flow-through column experiments using MRI. The student will develop MRI pulse sequences to image the various phases inside of a flow-through column. The student will also develop a flow-through column setup that allows us to vary moisture and NAPL content inside the column. In the next year we expect to complete development of the MRI pulse sequences and development of the column setup. In the following year multiple experiments will be imaged and analyzed with the developed algorithm.

A full-time graduate research assistant will be hired in the summer or Fall of 2000 to begin development of a mathematical model that accounts for pore-scale variations in residual NAPL and water. In the next year this student will begin by modifying an existing one-dimensional model of vapor-phase transport to account for the impact of spatially variable relative humidity upon sorption. The model results will be validated through comparison with laboratory experiments.

Advanced Experimental Analysis of Controls on Microbial Fe(III) Oxide Reduction

Project ID: 55164

Dr. Eric E. Roden, University of Alabama

Matilde M. Urrutia, University of Alabama

Research Objectives

Understanding factors which control the long-term survival and activity of Fe(III)-reducing bacteria (FeRB) in subsurface sedimentary environments is important for predicting the ability of these organisms to serve as agents for bioremediation of organic and inorganic contaminants. This project seeks to refine our quantitative understanding of microbiological and geochemical controls on bacterial Fe(III) oxide reduction and growth of FeRB, using laboratory reactor systems which mimic to varying degrees the physical and chemical conditions of subsurface sedimentary environments. Methods for studying microbial Fe(III) oxide reduction and FeRB growth in experimental systems which incorporate advective aqueous phase flux are being developed for this purpose. These methodologies, together with an accumulating database on the kinetics of Fe(III) reduction and bacterial growth with various synthetic and natural Fe(III) oxide minerals, will be applicable to experimental and modeling studies of subsurface contaminant transformations directly coupled to or influenced by bacterial Fe(III) oxide reduction activity.

Research Progress and Implications

This report summarizes research accomplished after approximately 2.5 yr of a 3-yr project. A central hypothesis of the research is that advective elimination of the primary end-product of Fe(III) oxide reduction, Fe(II), will enhance the rate and extent of microbial Fe(III) oxide reduction in open experimental systems. This hypothesis is based on previous studies in our laboratory which demonstrated that association of evolved Fe(II) with oxide and FeRB cell surfaces (via adsorption or surface precipitation) is a primary cause for cessation of Fe(III) oxide reduction activity in batch culture experiments [6].

Semicontinuous culturing was adopted as a first approach to test the above hypothesis [4]. Synthetic goethite or natural Fe(III) oxide-rich subsoils were used as Fe(III) sources, with the Fe(III)-reducing bacterium *Shewanella alga* as the test organism. Average residence times of 18 or 9 d were established by replacing a portion of the aqueous phase of the cultures with fresh sterile, anaerobic culture medium every 3-4 d. Consistent with our basic hypothesis, medium replacement resulted in a 2-4 fold increase in the cumulative amount of Fe(II) produced in the cultures over a 2-month incubation period, relative to that occurring in parallel batch cultures. In addition, Fe(III) reduction in the semicontinuous cultures showed little or no sign of slow-down at the end of the experiment, whereas reduction had virtually ceased in the batch cultures. In all cases the enhanced reduction was accounted for by generation of dissolved Fe(II) which was periodically removed from the cultures during aqueous phase replacement. The Fe(II) content of the solid-phase (sorbed or precipitated) was lower in the semicontinuous, which suggested that aqueous phase flux led to significant Fe(II) desorption or reduced solid-phase association. Together these results indicated that the primary basis for the stimulation of Fe(III) oxide reduction was advective removal of Fe(II). Measurements of bacterial protein in the cultures indicated that advective removal of Fe(II) stimulated bacterial growth, which is consistent with the observed persistence of Fe(III) oxide reduction activity. A simulation model in which Fe(II) sorption to the solid-phase resulted in blockage of surface reduction sites captured the contrasting behavior of the batch vs. semicontinuous Gt reduction systems.

A long-term (5 months) flow-through column experiment was conducted to test the hypothesis that advective Fe(II) removal could allow for complete microbial reductive dissolution of a crystalline Fe(III) oxide [5]. Such complete removal of Fe(III) oxide content has been documented in landfill leachate-contaminated aquifer sediments in Denmark [1]. The results showed that greater than 90% of the Fe content of synthetic goethite-coated sand was reduced and mobilized from the column as aqueous Fe(II) over the course of experiment. In contrast, only ca. 15% of the goethite-coated sand was reduced in parallel batch cultures. The near-complete removal of the Fe(III) oxide content of the goethite-coated sand was verified by total Fe determinations conducted on the contents of the columns at the conclusion of the experiment. Because of the very short residence time in the column reactors (6 hr), this experiment must be viewed as a 'proof of concept' rather than a simulation of in situ subsurface environments. Nevertheless, the findings are very important in that they show for the first time that crystalline Fe(III) oxides can, under the appropriate conditions, be completely reduced and solubilized through bacterial activity. This is in strong contrast to previous studies of crystalline Fe(III) oxide reduction, which typically revealed only relative minor degrees of reduction/solubilization.

In an attempt to more realistically model subsurface sedimentary environments, we conducted another dynamic flow experiment in which larger (3.8 cm diameter, 120 cm^3 internal volume) columns were packed with natural Fe(III) oxide-coated sand (from Abbott's Pit in VA) and pulse-inoculated (8 hour loading period) with FeRB cells to total volume-averaged concentration of 10^6 per mL. The reactors were designed after those developed recently by Roychoudhury et al. [7] for studies of aquatic sediment metabolism. The end-pieces of the reactors were fitted with a diffuser plate to encourage even distribution of fluid/solute flow through the reactor. The residence time in the column reactor was approximately 10 days, still relatively short but much more realistic in terms of natural groundwater aquifer systems. In this experiment, Fe(III) oxide reduction activity (as measured by the cumulative production of aqueous Fe(II) which exited the column) persisted throughout the 2.5-month incubation period. In strong contrast, reduction activity ceased after ca. 2 weeks in parallel batch culture experiments conducted with the same material. These results affirm those from the semicontinuous culture experiments which suggest that advective aqueous phase flux which leads to residence times on the order of weeks to months could play an important role in sustaining microbial Fe(III) oxide reduction in subsurface environments. In addition, our successful deployment of this experimental methodology gives us confidence that the approach can be used effectively in future studies of contaminant metal/radionuclide transformations coupled to bacterial Fe(III) oxide reduction. We have recently proposed to use this methodology for studies of Sr immobilization coupled to carbonate mineral formation during Fe(III) oxide reduction in subsurface sediment materials from Hanford and Oak Ridge National Laboratory [3]. This proposal contains a summary of important findings from this project as well as the Ferris/Roden EMSP 96-10 project on Sr immobilization under Fe(III) oxide-reducing conditions.

Our findings to date demonstrate that aqueous phase transport and attendant elimination of reaction end-products could play an important role in governing the *in situ* rate and persistence of microbial Fe(III) oxide reduction activity in anaerobic subsurface sediments. This in turn may have an important impact on the survival and activity of FeRB to be exploited for bioremediation purposes (e.g. the reductive immobilization of uranium, chromium, cobalt, and other metal/radionuclide contaminants; oxidation of hydrocarbon contaminants; reductive dechlorination of chlorinated solvents). An important implication of these findings is that models describing bacterial Fe(III) oxide reduction in subsurface environments will have to account for the fate of evolved Fe(II), and relate this in some manner to the abundance of available Fe(III) reduction sites and the viability of Fe(III)-reducing bacteria. A provisional model with these characteristics has been developed [4].

Several additional significant research accomplishments have been supported by this project, including:

(1) Two previous lines of research on the geochemical and microbiological controls on bacterial Fe(III) oxide reduction in batch culture, which were originally supported by a subcontract through Battelle PNNL, have been brought to completion during the course of the EMSP 96-10 project. This has resulted in publication of one paper [9] and submission of another [10].

(2) We have conducted a detailed analysis of the growth rate and biomass yield (derived from measurements of cell protein production) of two representative FeRB (*S. alga* and *Geobacter metallireducens*) growing with different forms of synthetic Fe(III) (Fe(III)-citrate, Fe(III)-EDTA, Fe(III)-NTA, amorphous $Fe(OH)_3$, α-FeOOH) as an electron acceptor [8]. Results indicate that despite considerable differences in the rate and pattern of Fe(III) reduction and FeRB growth, an approximately consistent long-term biomass yield of 5 to 15 mg protein per mmol Fe(III) reduced was observed with the different forms of Fe(III). These results provide a useful point of departure for quantitative modeling of FeRB growth and metabolism in various types of experimental and *in situ* anaerobic sedimentary systems. They also point to an unusual temporal offset between cell division and protein biosynthesis during growth of FeRB on solid-phase Fe(III), which we are currently examining in detail.

(3) We have tested the use of ^{3}H-leucine incorporation as a means of determining short-term (1-2 hr time frame) FeRB (*G. metallireducens* and *S. alga*) growth rates during reduction of soluble and solid-phase Fe(III). Results suggest that *G. metallireducens*, unlike *S. alga*, lacks the ability to express a high rate of exogenous leucine incorporation (probably due to the lack of an "active" cell membrane leucine uptake system). An important implication of this finding is that ^{3}H-leucine incorporation may not be an appropriate means of estimating FeRB growth rates in natural sediments in which *Geobacter* dominates Fe(III) reduction activity. Another important implication of this study is that rates of *S. alga* biomass production estimated from ^{3}H-leucine incorporation with 10-1000 nM total leucine concentration were much lower than those inferred from independent measurements of biomass yield during Fe(III) reduction, probably because of isotope dilution by *de novo* leucine biosynthesis. A subsequent experiment indicated that additions of at least 1 mM total leucine are required to repress *de novo* biosynthesis during short-term (0.5-2 hr) ^{3}H-leucine incorporation experiments in culture medium. Rates of protein production during growth of *S. alga* on ferric citrate estimated from ^{3}H-leucine incorporation with 1 mM total leucine agreed within a factor of 2 with independent estimates of bacterial protein production. This result indicates that ^{3}H-leucine incorporation can provide a quantitatively valid method for tracking instantaneous bacterial growth rates in experimental Fe(III) reduction systems.

(4) We are conducting a detailed comparison of the heterogeneity in reactivity of synthetic vs. natural Fe(III) oxides toward microbial reduction activity and abiotic reductive dissolution (by ascorbate at acidic pH; [2]). Results indicate that both chemical and biological Fe(III) oxide reduction can be described by first-order kinetics, and therefore data generated in our experiments can be analyzed in terms of the reactive continuum model described by Postma [2]. Initial results indicate that the apparent degree of heterogeneity in oxide reactivity is greater in relation to chemical vs. microbiological reduction mechanisms. These findings have important implications for development of quantitative kinetic models of Fe(III) oxide reduction activity in subsurface environments.

Planned Activities

Manuscripts on the column Fe(III) oxide reduction experiment and the FeRB growth/biomass production study are in preparation and will be submitted for publication by September 1999. Completion of two papers dealing with ^{3}H-leucine incorporation by FeRB and the use of ^{3}H-leucine incorporation to measure FeRB growth rates is anticipated by the end of the year. A broad-ranging study of the reduction kinetics of natural and synthetic Fe(III) oxide reduction, as influenced by heterogeneity of Fe(III) oxide reactivity (see (4) above) is underway and will be completed in 1999. We also plan to conduct one additional long-term (6 months) experiment on Fe(III) oxide reduction and FeRB growth rates (determined using ^{3}H-Leu) in flow-through column reactors. This experiment is intended to verify the influence of aqueous phase Fe(II) flux on the long-term persistence of Fe(III) oxide reduction activity and FeRB viability.

References

1. Heron, G., C. Crouzet, A. C. M. Bourg, and T. H. Christensen. 1994. Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques. Environ Sci Technol. 28:1698-1705.
2. Postma, D. 1993. The reactivity of iron oxides in sediments: a kinetic approach. Geochim. Cosmochim. Acta. 57:5027-5034.
3. Roden, E. E., F. G. Ferris, M. R. Leonardo, C. Zheng, and D. S. Smith. 1999. Geochemical retardation of subsurface strontium migration via carbonate mineral formation coupled to microbial Fe(III) oxide reduction.
4. Roden, E. E., and M. M. Urrutia. 1999. Ferrous iron removal promotes microbial reduction of crystalline iron(III) oxides. Environ. Sci. Technol. 33:1847-1853.
5. Roden, E. E., M. M. Urrutia, and C. J. Mann. 1999. Near-complete bacterial reductive dissolution of crystalline Fe(III) oxide under conditions of advective aqueous phase flux. Manuscript in preparation.
6. Roden, E. E., and J. M. Zachara. 1996. Microbial reduction of crystalline Fe(III) oxides: role of oxide surface area and potential for cell growth. Environ. Sci. Technol. 30:1618-1628.
7. Roychoudhury, A. N., E. Viollier, and P. VanCappellen. 1998. A plug flow-through reactor for studying biogeochemical reactions in undisturbed aquatic sediments. Appl. Geochem. 13:269-280.
8. Urrutia, M. M., and E. E. Roden. 1998. Growth rates and biomass production of dissimilatory Fe(III)-reducing bacteria with soluble and solid-phase Fe(III). Manuscript in preparation.
9. Urrutia, M. M., E. E. Roden, J. K. Fredrickson, and J. M. Zachara. 1998. Microbial and geochemical controls on synthetic Fe(III) oxide reduction by Shewanella alga strain BrY. Geomicrobiol. J. 15:269-291.
10. Urrutia, M. M., E. E. Roden, and J. M. Zachara. 1999. Influence of aqueous and solid-phase Fe(II) sinks on microbial reduction of crystalline Fe(III) oxides. Environ. Sci. Technol. Submitted for publication.

Information Access

Roden, E.E. and M.M. Urrutia. 1999. Ferrous iron removal stimulates microbial iron(III) oxide reduction in semicontinuous cultures. *Environ. Sci. Technol*. 33:1847-1853.

Urrutia, M.M., E.E. Roden, J.K. Fredrickson, and J.M. Zachara. 1998. Microbial and surface chemistry controls on reduction of synthetic Fe(III) oxide minerals by the dissimilatory iron-reducing bacterium *Shewanella alga. Geomicrobiol. J.* 15:269-291.

Urrutia, M.M., E.E. Roden, and J.M. Zachara. Influence of aqueous and solid-phase Fe(II) complexants on microbial reduction of crystalline Fe(III) oxides. *Environ. Sci. Technol.* April 1999.

Roden, E. E., F. G. Ferris, M. R. Leonardo, C. Zheng, and D. S. Smith. 1999. Geochemical retardation of subsurface strontium migration via carbonate mineral formation coupled to microbial Fe(III) oxide reduction. Proposal submitted to U.S. Department of Energy, Office of Science, Notice 99-06, Environmental Management Science Program, Research Related to Subsurface Contamination/Vadose Zone Issues.

Urrutia, M.M. and E.E. Roden. 1997. Growth rates and biomass production of dissimilatory Fe(III)-reducing bacteria with soluble and solid-phase Fe(III). American Society for Microbiology, 97th Annual Meeting, Abstract Volume, p. 337.

Roden, E.E. and M.M. Urrutia. 1997. Microbial Fe(III) oxide reduction in aquatic sediments: new insights into controls and quantitative significance in biogeochemical fluxes. XIII International Symposium on Environmental Biogeochemistry, Abstract Volume, p. 211.

Roden, E.E. and M.M. Urrutia. 1998. Microbial Fe(III) oxide reduction in open experimental systems. American Society for Microbiology, 98th Annual Meeting, Abstract Volume, p. 409.

May, T. and E.E. Roden. ^{3}H-leucine incorporation by Fe(III)-reducing bacteria. American Society for Microbiology, 98th Annual Meeting, Abstract Volume, p. 409.

Containment of Toxic Metals and Radionuclides in Porous and Fractured Media: Optimizing Biogeochemical Reduction Versus Geochemical Oxidation

Project ID: 55267

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Research Objectives

The purpose of this research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that subsurface microbial activity can effectively alter the redox state of toxic metals and radionuclides so that they are immobilized for long time periods. Our objectives are to (1) develop an improved understanding of the rates and mechanisms of competing geochemical oxidation and microbiological reduction reactions that govern the fate and transport of redox-sensitive metals and radionuclides (i.e. Cr, U, and Co-EDTA) in the subsurface, and (2) quantify the conditions that optimize the microbial reduction of toxic metals and radionuclides, for the purpose of contaminant containment and remediation in heterogeneous systems that have competing geochemical oxidation, sorption, and organic ligands. The overall goal of this project is to use basic research to develop a cost effective remediation strategy that employs *in situ* contaminant immobilization. Specifically, we will develop active biowall technologies to contain priority EM contaminant plumes in groundwater.

Research Progress and Implications

This report summarizes 3 years of research for a 3-year project.

To date, we are one of the first research groups to demonstrate the sustained microbial reduction of ^{60}Co(III)EDTA to ^{60}Co(II)EDTA under dynamic flow conditions. The net reduction of the ^{60}Co(III)EDTA dominates the fate and transport of this contaminant, even in the presence of strong mineral oxidants commonly found in the subsurface (e.g. Mn- and Fe-oxides). The environmental implications of these findings are pronounced since ^{60}Co(III)EDTA is extremely stable and soluble, and this enhances its persistence and transport in subsurface environments. By discovering a way to keep the bacteria healthy and growing, we were able to effectively stabilize ^{60}Co(II)EDTA in a flowing subsurface system. This is advantageous from a remedial perspective since ^{60}Co(II)EDTA is a weaker complex than ^{60}Co(III)EDTA, and therefore easier to decouple and remediate. The research findings, published by Brooks et al. (1999, ES&T), provide new and important information on how to successfully implement a bioreduction strategy at the field scale. Their use of a dynamic flow system with sustained bacterial growth conditions in geochemically reactive media is consistent with contaminant migration scenarios *in situ*. Within this subtask we have also used synchrotron based radiation (X-ray Absorption Near Edge Structure - XANES) to identify the mechanisms and reaction pathways involved in the mineral catalyzed oxidation of ^{60}Co(II)EDTA to ^{60}Co(III)EDTA (Fendorf et al., 1999, GCA). By quantifying the kinetics and mechanisms of the redox reaction, an accurate numerical formulation of the processes was performed and the system was rigorously modeled (Saiers et al., 2000, WRR).

The fate and transport of U(VI) in ORNL, Savannah River, and Hanford sediments have been quantified for a variety of environmental conditions. Investigations emphasized the effects of

geochemical oxidation and interfacial sorption reactions, and the effects of biological reduction processes on the time-dependent mobility of U in the subsurface media. The bacterial reduction of U(VI) was found to be quite rapid, with time scales on the order of minutes to hours (Zhang et al., 2000). The reduction of U(VI) is advantageous from an environmental perspective since reduced U(IV) is significantly less soluble and less mobile in subsurface environments relative to the oxidized species. A unique aspect of this research was our use of time-resolved X-ray Absorption Spectroscopy (XAS) located at the Stanford Synchrotron Radiation Laboratory, in Stanford CA. Since this technique is sensitive to metal redox shifts and interfacial surface reactions, we used XAS to quantify the time-dependent bacterial reduction of U(VI) to U(IV). Often times geochemical sorption reactions dominate U(VI) dynamics. We have found that U(VI) sorption on ORNL, Hanford, and Savannah River sediments is highly dependent on pH and pCO_2. Classic U(VI) adsorption envelopes were observed with adsorption edges increasing sharply from pH 4 to 6 and then decreasing sharply from pH 7 to 8. Sorption k_d values range from ~50 cm^3/g at pH 4 and 8 to nearly 2000 cm^3/g at pH 6-7. Above pH 7, U-CO_3 species dominated the equilibrium solution and they were less retarded than U(VI) and its hydrolysis products (Barnett et al., 2000, SSSAJ). Wielinga et al. found that the presence of soils and sediments significantly decreases the rate of U(VI) bioreduction.

The fate and transport of Cr(III) and Cr(VI) in ORNL, Savannah River, and Hanford sediments were quantified for a variety of environmental conditions (Jardine et al., 1999, ES&T, 2000, SSSAJ). The reduction of Cr(VI) to Cr(III) is desirable from an environmental perspective since Cr(VI) is a potent carcinogen and highly mobile in the environment, whereas Cr(III) is significantly less soluble and less toxic. The bacterial reduction of Cr(VI) to Cr(III) can be problematic due to the toxicity associated with the oxidized form of this contaminant. Nevertheless, we have succeeded in quantifying the direct bacterial reduction of Cr(VI) to Cr(III) by previously described metal-reducing microorganisms as well as by novel isolates that we have discovered from a contaminated field site at Oak Ridge. These research findings provide new and important information on how to successfully implement a bioreduction strategy at the field scale. In addition, we have employed two alternative routes to reduce Cr(VI). The first route is a direct geochemical mechanism, where surface bound natural organic carbon (NOM) is used to effectively reduce Cr(VI) to Cr(III) thereby slowing its subsurface mobility many orders of magnitude (Jardine et al., 1999, ES&T). XAS was used to quantify the immobilized Cr(III) product on the solid phase. This technique shows real promise for use in geochemical barriers since NOM sorbs extremely well to soils and sediments and serves as an efficient, cost effective means of immobilizing Cr. The second route involves an indirect biogeochemical mechanism where metal reducing bacteria reduce Fe(III)-oxides to Fe(II), where the latter quickly reduces Cr(VI) to Cr(III). The Fe(II) is simultaneously oxidized to Fe(III), which can be reduced by the microorganisms to participate in the cycle again (Fendorf, unpublished data).

Figure 1 Scott Brooks prepares anaerobic column flow experiment to investigate the bioreduction of toxic metals and radionuclides in reactive porous media.

By contrast, Cr(VI) that is reduced to Cr(III) remains in the less soluble and less toxic reduced form. The technique shows promise for use in active biowall technologies for the in-situ containment of Cr. The efficiency of both techniques for immobilizing Cr has been quantified using time-resolved XAS since this instrument probes for contaminants on the surface of sediments and bacteria, thereby permitting the determination of the contaminant chemical and structural state.

Peer-reviewed manuscripts and book chapters

Jardine, P.M., R. O'Brien, Wilson, G.V., and J.P. Gwo. 1998. Experimental techniques for confirming and quantifying physical nonequilibrium processes in soils. p. 243-271. (In) H.M. Selim and L. Ma. Physical Nonequilibrium in Soils: Modeling and Application. Ann Arbor Press, Inc. Chelsea, Michigan.

Gwo, J. P., and G. T. Yeh. 1997. Application of a parallel 3-dimensional hydrogeochemistry HPF code to a proposed waste disposal site at the Oak Ridge National Laboratory. In Tentner, A. (ed.), High Performance Computing 1997: Grand Challenges in Computer Simulation, p.128-133.

Fendorf, S.E., P.M. Jardine, D.L. Taylor, and S.C. Brooks. 1999. Auto-inhibition of oxide mineral oxidative capacity toward Co(II)EDTA: Time-resolved studies using XANES spectroscopy. (In) Sparks, D.L. and T. Grundel (eds.) Kinetics and mechanisms of sorption processes at the mineral-water interface. ACS Symposium Series 715. pp. 358-371.

Fendorf, S.E., P.M. Jardine, R.R. Patterson, D.L. Taylor, and S.C. Brooks. 1999. Pyrolusite surface transformations measured in real-time during the reactive transport of Co(II)EDTA. Geochim. Cosmochim. Acta. 63:3049-3057.

Brooks, S.C., S.L. Carroll, and P.M. Jardine. 1999. Sustained bacterial reduction of Co(III)EDTA$^-$ in the presence of competing geochemical oxidation during dynamic flow. Environ. Sci. Technol. 33:3002-3011.

Jardine, P.M., S.E. Fendorf, M.A. Mayes, I.L. Larsen, S.C. Brooks, and W.B. Bailey. 1999. Fate and transport of hexavalent chromium in undisturbed heterogeneous soil. Environ. Sci. Technol. 33:2939-2944.

Mahinthakumar, G., Gwo, J. P., and Moline G. R., 1999. Subsurface biological activity zone detection using genetic algorithms, ASCE J. of Environ. Eng. 125(2): 1103-1112.

Jardine, P.M., W.E. Sanford, J.P. Gwo, O.C. Reedy, D.S. Hicks, R.J. Riggs, and W.B. Bailey. 1999. Quantifying diffusive mass transfer in fractured shale bedrock. Water Resour. Res. 35:2015-2030.

Barnett, M.O., P.M. Jardine, S.C. Brooks, and H.M. Selim. 2000. Adsorption and transport of U(VI) in subsurface media. Soil Sci. Soc. Am. J. (in press).

Jardine, P.M., S.C. Brooks, G.V. Wilson, and W.E. Sanford. 1999. Basic research strategies for resolving remediation needs in contaminated fractured subsurface media. (In) Dynamics of Fluids in Fractured Rocks: Concepts and Recent Advances. (ed) B. Faybishenko. American Geophysical Union, Geophysical Monograph Series (in press).

Jardine, P.M., G.V. Wilson, R.J. Luxmoore, and J.P. Gwo. 1999. Conceptual Model of Vadose-Zone Transport in Fractured Weathered Shales. (In) Conceptual Models of Flow and Transport in the Fractured Vadose Zone. (ed) P.A. Hsieh. National Research Council (in press).

Gwo, J. P., E. F. D'Azevedo, H. Frenzel, M. Mayes, G. T. Yeh, P. M. Jardine, K. M. Salvage, and F. M. Hoffman, 1999. HBGC123D: A high performance computer model of coupled hydrogeological and biogeochemical processes, Computers and Geosciences. (in review).

Gwo, J. P. and R. O'Brien, 2000. On the search of preferential flowpaths in structured porous media using a simple genetic algorithm. Water Resour. Res. (in review).

Saiers, J.E., H. Guha, P.M. Jardine, and S.C. Brooks. 2000. Development and evaluation of a mathematical model for the transport and oxidation-reduction of CoEDTA. Water Resour. Res. (in review).

Jardine, P.M., T.L. Mehlhorn, S.E. Fendorf, and S.C. Brooks. 2000. Geochemical processes governing the fate and transport of Cr(III) and Cr(VI) in soils and sediments. Soil Sci. Soc. Am. J. (in preparation).

Fendorf, S.E., P.M. Jardine, and S.C. Brooks. 2000. Mechanisms of Cr(III) and Cr(VI) adsorption on soils and sediments using X-ray Absorption Spectroscopy. Soil Sci. Soc. Am. J. (in preparation).

Barnett, M. O., P. M. Jardine and S. C. Brooks. 2000. Uranium(VI) adsorption to heterogeneous subsurface media: Application of a surface complexation model. (in preparation).

Zhang, C., S.C. Brooks, S.E. Fendorf, and P.M. Jardine. 2000. Microbial uranium reduction and biomineralization: implication for immobilization of toxic metals and radionuclides Environ. Sci. & Technol. (in preparation).

Published abstracts and presentations

Fendorf, S., P.M. Jardine, and S.C. Brooks. 1997. Sorption induced inhibition of redox reactions involving manganese oxides. American Chemical Society. San Francisco, CA. April 13-17.

Mayes, M.A., O.C. Reedy, I.L. Larsen, S.C. Brooks, and P.M. Jardine. 1997. Multispecies contaminant transport in undisturbed columns of weathered fractured shale. American Society of Agronomy. Anaheim, CA. Oct. 26-31.

Sanford, W.E., and P.M. Jardine. 1997. Examining diffusion with multiple tracers to aid remediation of contaminated sites. American Society of Agronomy. Anaheim, CA. Oct. 26-31.

Mehlhorn, T.L., P.M. Jardine, S.C. Brooks, S.E. Fendorf, and J.E. Saiers. 1997. Geochemical processes governing the fate and transport of Cr(III) and Cr(VI) in soils. American Society of Agronomy. Anaheim, CA. Oct. 26-31.

Brooks, S.C., and P.M. Jardine. 1997. Bacterial reduction of toxic metals during dynamic flow. American Society of Agronomy. Anaheim, CA. Oct. 26-31.

Mayes, M.A., O.C. Reedy, I.L. Larsen, S.C. Brooks, and P.M. Jardine. 1997. Multispecies contaminant transport in undisturbed columns of weathered fractured shale. Geologic Society of America Oct.

Jardine, P.M., G.V. Wilson, W.E. Sanford, and R.J. Luxmoore. 1998. Exploring subsurface transport mechanisms in fractured media at laboratory and field scales. Conference on "Mass transport in fractured aquifers and aquitards" Geological Institute, Unversity of Copenhagen, Denmark, May 14-16, 1998.

Zhang, C., S. Brooks, S. Fendorf, and P. Jardine. 1998. Microbial uranium reduction and biomineralization: implication for immobilization of toxic metals and radionuclides. 17th annual meeting for International Mineralogical Association, Toronto, August.

Jardine, P.M. 1998. Can basic research on contaminant transport be used to improve the design of remedial strategies? Proceedings of "School of Environmental Science and Technology". Buenos Aires, Argentina. August 24-28.

Guha, H., J.E. Saiers, P.M. Jardine, and S.C. Brooks. 1998. Development and evaluation of a mathematical model for oxidation, sorption, and transport of Co(II)EDTA^{2-}. American Geophysical Union, Dec. 6-10, 1998, San Francisco, CA.

Gwo, J. P., and P. M. Jardine, Complexity in Hydrobiogeochemistry: A Multidisciplinary Integrative Approach, A minisymposium, the Fifth SIAM Conference on Mathematical and Computational Issues in the Geosciences, March 24-27, 1999, San Antonio, Texas (http://hbgc.esd.ornl.gov/pubs/siam99/).

Jardine, P.M., T.L. Mehlhorn, I.L. Larsen, S.C. Brooks, J.P. Gwo, G.V. Wilson, and W.E. Sanford. 1999. Basic research strategies for resolving remediation needs in contaminated fractured subsurface media. Symposium on Dynamics of Fluids in Fractured Rocks: Concepts and Recent Advances. Lawrence Berkeley National Laboratory. February 6-10, 1999, Berkeley, CA.

Frenzel, H., M. A. Mayes, J. P. Gwo, P. M. Jardine, and G. T. Yeh, 1999. Application of a hydrobiogeochemistry computer model to fate and transport of co-contaminants in fractured saprolite, AGU Fall Meeting, December 13-17, 1999, San Francisco, California.

Microbial Mineral Transformations at the Fe(II)/Fe(III) Redox Boundary for Solid Phase Capture of Strontium and Other Metal/Radionuclide Contaminants

Project ID: 54790

Dr. F. Grant Ferris, University of Toronto

Eric Roden, University of Alabama

Research Objective

Determine microbiological and geochemical controls on carbonate mineral preciptation reactions, and identify contributions of these processes to the solid phase capture of strontium and other metal/radionuclide contaminants. The study is relevant to the development of new clean-up strategies for DOE sites where strontium and other metal/radionuclides exist as ubiquitous and often mobile contaminants.

Research Progress and Implications

The work summarized in this report pertains to the final year of a three-year project investigating the use of bacteria to concentrate and immobilize Sr^{2+}, as well as other metal/radionuclide, contaminants. Major accomplishments over the first two years of the project included completion of sorption studies with bacteria and hydrous iron oxides (HFO), assessment of the impact of Sr^{2+} on bacterial Fe(III)-reduction, induction of carbonate mineral precipitation and solid phase capture of Sr^{2+} under Fe(III)-reducing conditions, and discovery of a procedure to attain rapid high-level concentration of Sr^{2+} in microbiologically produced calcite. In the past year, studies have focused on the influence of ionic strength on Sr^{2+} sorption by bacteria and HFO, the impact of Ca^{2+} as a competing ion in Sr^{2+} immobilization under iron-reducing conditons, and measurement of the extent of Sr^{2+} solid phase capture in saturated porous sand media in the presence of iron-reducing bacteria.

The sorption studies with iron-reducing bacteria and HFO established that the solid phase partitioning of Sr^{2+} at bacterial and HFO surfaces can be quantitatively described using surface complexation theory. These experiments documented further that the scavenging of Sr^{2+} is strongly pH dependent, showing rapid increases in Sr^{2+} sorption as pH increased; however, significant Sr^{2+} sorption occurs at the bacterial surfaces at much lower pH values than at the HFO surfaces, emphasizing their importance for contaminant modeling, and for possible remedial applications. In recent experiments, sorption of Sr^{2+} by bacteria was found to be extremely sensitive to ionic strength, whereas Sr^{2+} sorption by HFO was not affected. Moreover, composite mixtures of bacteria and HFO were found to exhibit Sr^{2+} sorption behavior intermediate between the pure bacteria and HFO, but showed a lower sorptive capacity than anticipated. This result is explained by a masking of bacterial sorption sites by the surface associated HFO, which has a lower relative sorptive capacity than the bacterial surface.

Other results indicate that the concentration of HFO precipitated at the bacterial surface will ultimately determine the scavenging ability of the bacteria-HFO complex. However, the fundamental concept is that microbial mediated reactions involving dissolved inorganic contaminants must be considered if accurate contaminant fate models are to be developed.

The potential for immobilization of aqueous Sr^{2+} coupled to microbial reduction of a synthetic crystalline Fe(III) oxide (goethite) was examined using a bicarbonate-buffered anaerobic artificial groundwater, containing 1.0 mM, 0.1 mM, or 0.01mM Sr^{2+}. Experiments were also conducted using 10 mM Ca^{2+} simulate a natural Ca-rich groundwater. Although Fe(III) reduction was initially slower

in Ca-amended cultures, the overall amount reduction was similar in both systems. In the Ca-containing cultures, there was only modest removal (20-30%) of Sr^{2+} from solution, despite the removal of a significant amount of Ca^{2+} (5-9 mM) through the formation of $CaCO_3$. The pH remained constant at 6.8-6.9 in these cultures due to buffering of the system by $CaCO_3$ precipitation. In contrast, pH rose to much higher levels in the cultures without Ca, and a much greater amount of Sr was immobilized. At all three levels of Sr in the absence of Ca^{2+}, 90 % of aqueous Sr was removed after 51 days of incubation. Between 10 and 15 mmol/L solid phase carbonate was formed in the cultures, which presumably accounted for the Sr^{2+} immobilized during Fe(III) oxide reduction. In the 0.1 mM and 0.01mM Sr cultures there was an initial release of sorbed Sr as Fe(III) was reduced, followed by subsequent Sr immobilization. In the 1.0 mM Sr^{2+} - Ca^{2+}-free cultures, there was immediate solid-phase capture of Sr^{2+}. This initial sorption and release was not observed in the 1.0 mM Sr systems due to saturation of sorption sites.

In saturated sand, the extent of Fe (III) reduction was not changed; however, sand enhanced the rate and extent of subsequent removal of Sr^{2+} from solution. These findings demonstrate the potential for solid-phase capture of Sr during carbonate formation coupled to microbial reduction of HFO and crystalline Fe(III) oxide which are common to many soil and subsurface sedimentary environments. This process may provide a mechanism for retarding the migration of Sr in carbonate-rich groundwater aquifers.

Demonstration of Sr^{2+} solid phase capture during Fe(III) reduction suggests that considerable potential exists to adapt this novel immobilization concept to the development of new clean-up strategies for DOE sites where strontium and other metal/radionuclides exist as ubiquitous and often mobile contaminants. Further laboratory and field investigations focused on assessement of performance under *in situ* conditions are considered to be the most appropriate course of action.

Planned Activities

There are two graduate students presently working on the project that are in the final stages of their thesis research (one each at the University of Alabama and the University of Toronto). Several manuscripts are expected to be prepared for journal submission based on the work of these students. In order for these students to complete their work and write papers, a no cost extension has been requested. Two new EMSP proposals have been submitted based on the results of this project, one through the University of Alabama and the other through INEEL where groundwater and vadose zone Sr^{2+} contamination is recognized as a problem.

Information Access

1. Howell, J.R. 1998. Effects of microbial Fe(III) oxide reduction on pH, DIC, and carbonate mineral formation: implications for metal mobility. M.S. Thesis, Department of Geology, University of Alabama, Tuscaloosa, AL 35487.
2. Warren, L.A. and F.G. Ferris. 1998. Solid phase partitioning of uranium and copper in the presence of HFO and bacteria. In, Proceedings 9th International Symposium on Water Rock Interaction WRI-9 (G.B. Arehart and J.R. Hulston, eds.), Balkema, Rotterdam. pp. 115-117.
3. Howell, J.R., R.J. Donahoe, E.E. Roden, and F.G. Ferris. 1998. Effects of microbial iron oxide reduction on pH and alkalinity in anaerobic bicarbonate-buffered media: implications for metal mobility. Mineralogical Magazine 62A: 657-658. (N)
4. Leonardo, M.R., F.G. Ferris, and E.E. Roden. Immobiliztion of strontium during carbonate mineral formation coupled to microbial reduction of amorphous Fe(III) oxide. Submitted to Environmental Science and Technology.
5. Parmar, N., L.A. Warren, E.E. Roden, and F.G. Ferris. Solid phase capture of strontium by the iron reducing bacteria Shewenella alga. Submitted to Chemical Geology (04/99)
6. Small, T.D., L.A. Warren, E.E. Roden, and F.G. Ferris. Strontium sorption to bacterial and Fe oxide surfaces. Submitted to Environmental Science and Technology. (05/99)
7. Warren, L.A., P. Maurice, and F.G. Ferris. Strontium, uranyl, and copper incorporation in bacterially mediated calcite precipitation. In preparation for Environmental Science and Technology.
8. Warren, L.A., N. Parmar, and F.G. Ferris. 1998. Strontium, uranyl, and copper incorporation in bacterially mediated calcite precipitation. . Geological Socieity of America Annual Meeting, Toronto.
9. Parmar, N., L.A. Warren, and F.G. Ferris. 1998. Solid phase capture of strontium by the iron reducing bacteria Shewenella alga. . Geological Socieity of America Annual Meeting, Toronto.
10. Small, T.D., L.A. Warren, and F.G. Ferris. 1998. Strontium sorption to bacterial and Fe oxide surfaces. . Geological Socieity of America Annual Meeting, Toronto.

11. Maurice, P.A., L.A. Warren, F.G. Ferris. 1998. Calcite precipitation by B. pasteurei: AFM imaging of microbial-mineral interactions. Geological Society of America Annual Meeting, Toronto.

Reduction and Immobilization of Radionuclides and Toxic Metal Ions Using Combined Zero Valent Iron and Anaerobic Bacteria

Project ID: 55071

Dr. Lenly Weathers, Tennessee Technological University

Research Objectives

Large groundwater plumes contaminated with toxic metal ions, including radionuclides, exist at several DOE facilities. Previous research indicated that both zero valent iron and sulfate reducing bacteria can yield significant decreases in concentrations of redox sensitive metals and radionuclides due to abiotic and biotic reduction, respectively. The major hypothesis of this research is that a combined abiotic-biological system can synergistically combine both processes to maximize metal ion reduction in an engineered permeable reactive barrier. The second major hypothesis is that design of either in situ or ex situ metal ion reduction processed based on biotic, abiotic or combined abiotic/biotic reduction scheme requires a more thorough understanding of the rates of the reaction and quantification of the parameters which impact the rates of reduction. A natural corollary to this hypothesis is that this increased understanding must also include quantification of parameters or parameter levels which inhibit either the biotic or abiotic process. The overall goal of this project is to design a combined abiotic/biotic, reactive, permeable, in situ barrier with sufficient reductive potential to prevent downgradient migration of toxic metal ions.

Research Progress

Successful completion of this goal required evaluating (1) the kinetics of abiotic metal ion reduction under a range of environmental conditions and (2) the kinetics of biotic processes under a range of environmental conditions.

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

Project ID: 70165

Fred Brockman, Pacific Northwest National Laboratory

Christopher Murray, Pacific Northwest National Laboratory
John Selker, Oregon State University
Peter Bottomley, Oregon State University

Research Objectives

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

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

The specific project objectives are to:

(1) Determine the occurrence and distribution of denitrifiers and methanotrophs in the deep vadose zone at the DOE Hanford Site,
(2) Determine bioreactor kinetics for carbon tetrachloride removal in the presence of methane, nitrous oxide, and triethyl phosphate by denitrifiers (carbon tetrachloride to chloroform) and methanotrophs (chloroform to carbon dioxide) isolated from the field site,
(3) Determine the rate and extent of microbial colonization in response to gas-phase nutrient injection, and
(4) Use the above information to develop an improved vadose zone reactive transport model, and explore the level of site heterogeneity information that is needed for accurate premodeling of attenuation of vadose zone contaminant transport by engineered bioremediation.

Research Progress and Implications

This report summarizes work after 6 months of a 3-year project. Field samples are required to address specific objectives 1 and 2. Due to cost considerations, we must obtain samples from coring activities being conducted by other programs. We are working with DOE-Richland to identify opportunities to obtain vadose zone samples near and within the carbon tetrachloride- contaminated zone at the Hanford Site. The best near-term opportunity appears to be with the Innovative Treatment Remediation Demonstration (ITRD) program.

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

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

Planned Activities

Specific objectives 1 and 2: Continue to work with DOE to identify sampling opportunities and obtain pertinent field samples.

Specific objective 3: Studies have been initiated to examine the ability of strain KC to colonize vadose zone sediment (from a single inoculation point) as a function of varying (a) water-filled porosity, (b) pore throat size, (c) aqueous nutrient concentration, and (d) distance from a nutrient injection point (FY2000). Studies will be extended in FY2001 to examine colonization as a function of important vadose zone hydrological processes such as funnel flow along inclined textural interfaces.

Specific objective 4: Use experimental results from specific objective 3 to further develop and validate the biological component of STOMP.

Information Access

None to date (project is 6 months old)

Biodegradation of Chlorinated Solvents: Reactions Near DNAPL and Enzyme Function

Project ID: 70063

Dr. Perry L. McCarty, Stanford University

Research Objectives

Chlorinated solvents are among the most common organic chemical groundwater contaminants at DOE sites, as well as at DOD and industrial facilities. Included are the solvents trichloroethene (TCE), tetrachloroethene (PCE), and carbon tetrachloride (CT). Commonly these contaminants occur as dense non aqueous phase liquids (DNAPLs) that continue to contaminate groundwater as it moves through the DNAPL location. Also, commonly, these contaminants are associated with other contaminants of concern. An example is the Hanford site where nitrates, tritium, and carbon tetrachloride co-mingle in significant plumes. The objective of this study is to obtain basic information on processes affecting the in situ biodegradation of the above chlorinated solvents and their degradation daughter products, especially near the DNAPL source where concentrations are exceptionally high. Here, we have found anaerobic biological processes provide the best opportunity for efficient in situ biodegradation because the high concentrations of solvents and daughter products tend to be inhibitory to other microorganisms, such as methanogens, that compete for electron donor that may be added to enhance this process. We have laboratory cultures that are capable of degrading saturation concentrations of PCE, and are cooperating with DuPont Chemical Corporation, who has several mixed cultures, as well as molecular probes, that will be useful in this study. The study will be conducted in three separate phases. In the first, the kinetics of chlorinated solvent biodegradation at or near saturation concentrations will be investigated. Important here is the potential for inhibition by individual chlorinated solvents and end products, as well as those of potential co-contaminants. The second phase is to develop a better understanding of the underlying biochemical processes involved in key enzymatic reactions, such as the dehalogenation of vinyl chloride. From these studies, molecular probes that can detect the presence and activity of dehalogenating enzyme activity will be developed for field application. The third phase is concerned with obtaining better basic knowledge of a highly unique denitrifying bacteria (Pseudomonas stutzeri strain KC) that degrades carbon tetrachloride without producing chloroform as a hazardous intermediate. We have successfully field tested bioaugmentation for CT degradation with this organism, and have the genes involved in synthesis of the cellular component that carries out this interesting process. With the further development here proposed, we will gain an understanding of what conditions are required to produce the dehalogenating factor and how best to apply this organism or the dehalogenating factor it produces for in situ biodegradation of carbon tetrachloride. The three phases represent an integrated approach to addressing an important in situ remediation process.

Stable Isotopic Investigations of In-Situ Bioremediation of Chlorinated Organic Solvents

Project ID: 55388

Neil C. Sturchio, Argonne National Laboratory

Research Objectives

The new scientific information generated by this research focuses on the problem of the environmental management of chlorinated solvents. The results of this research have yielded a new tool that will significantly improve the understanding of the fate and transport of chlorinated solvents in ground water aquifers and vadose zones, which can translate into large savings of cleanup costs.

The principal benefits to DOE of the new information generated are that: (1) it will improve site characterization by revealing the nature and extent of natural attenuation processes occurring at a site and can be used in conjunction with hydrologic data to estimate attenuation rates and (2) it can be used to monitor cleanup and to help evaluate the most effective engineered remedial strategy for a given site.

The research objectives of this program are threefold: to develop methods for measuring stable isotope ratios of carbon and chlorine in chlorinated aliphatic hydrocarbons (CAHs); to apply these methods to experimental determinations of kinetic and equilibrium isotope effects during biological, chemical, and physical transformation of CAHs; and to apply these methods to CAHs extracted from ground water at well-characterized, contaminated aquifer sites. The overall objective is to develop an understanding of the environmental isotopic behavior of CAHs and to apply this understanding to better characterize, monitor, and evaluate natural and engineered bioremediation. This is an important problem because of the magnitude and frequency of ground water contamination by CAHs and the resultant health risks imposed to the population, as well as the enormous costs involved in cleaning up such contamination.

Research Progress and Implications

This project was completed in September, 1999. This project is innovative as it represents the first systematic effort of its kind. Since its inception, a number of other scientists have also started research into the stable isotope chemistry of CAHs in both laboratory and field investigations . Complementary experimental and theoretical studies of the equilibrium stabilities and kinetics of CAH degradation by microbial and abiotic mechanisms continue to be a major field of research. This research has advanced our understanding of the isotope effects associated with biological, chemical, and physical transformations of the CAHs. It has advanced our knowledge of the extent to which various processes affect the isotopic composition of chlorinated solvents in ground water aquifers. We have applied our methods to the analysis of CAH in a number of contaminated aquifers having contrasting hydrogeologic characteristics and treatment histories, resulting in valuable insights into the extent and mechanisms of natural and engineered remediation. Additional scientific hurdles include: (1) establishing a larger database of experimentally measured kinetic isotope effects for microbial degradation of chlorinated solvents and (2) integrating isotopic data more fully into conceptual and numerical ground water and vadose zone transport models for chlorinated solvents.

Planned Activities

N/A (project completed).

Information Access

Holt B. D., Sturchio N. C., Abrajano T. A., and Heraty L. J, 1997. Conversion of chlorinated organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. *Analytical Chemistry* **69**, 2727-2733.

Sturchio N. C., Clausen J. C., Heraty L. J., Huang L., Holt B. D., and Abrajano T., 1998. Stable chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer. *Environmental Science and Technology* **32**, 3037-3042.

Dayan, H., Abrajano T., Sturchio N. C., and Winsor L., 1999. Carbon isotopic fractionation during reductive dechlorination of chlorinated solvents by metallic iron. *Organic Geochemistry* **30**, 755-763.

Heraty L. J., Fuller M. E., Huang L., Abrajano T., and Sturchio N. C., 1999. Carbon and chlorine isotopic fractionation during microbial degradation of dichloromethane. *Organic Geochemistry* **30**, 793-799.

Huang L., Sturchio N. C., Abrajano T., Heraty L., and Holt B. D., 1999. Carbon and chlorine isotope fractionation of chlorinated aliphatic hydrocarbons by evaporation. *Organic Geochemistry* **30**, 777-785.

Sturchio N. C., Heraty L., Holt B. D., Huang L., Abrajano T., and Smith G., 2000. Stable isotope ratios of chlorinated aliphatic hydrocarbons in contaminated aquifers. *Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, May 22-25, 2000.

Additional Information

U. S. Patent # 5,942,439. Ben D. Holt and Neil C. Sturchio. *Method for Isotopic Analysis of Chlorinated Organic Compounds* (issued 8/28/1999).

Design and Development of a New Hybrid Spectroelectrochemical Sensor; Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone

Project ID: 54674; 70010

William R. Heineman; University of Cincinnati

Carl J. Seliskar; University of Cincinnati
Thomas H. Ridgway; University of Cincinnati
Samuel A. Bryan; Pacific Northwest National Laboratory
Timothy L. Hubler; Pacific Northwest National Laboratory

Research Objective

The general objective is the design and implementation of a new sensor technology that offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at DOE sites nationwide. The specific objectives are threefold: demonstration of the general sensor concept on a variety of model systems; development of a sensor for ferrocyanide with testing on waste tank simulant; and development of a sensor for pertechnetate applicable to the Vadose Zone.

Research Progress and Implications

This report summarizes work after $3^1/_2$ years on the general development of the sensor concept with model systems and of the sensor for ferrocyanide and work after $^1/_2$ year on the pertechnetate sensor.

The spectroelectrochemical sensor embodies two modes of instrumental selectivity (electrochemical and spectroscopic) in addition to selective partitioning into a chemically-selective film. The sensor consists of a planar optical substrate/electrode coated with the selective film. Sensing of analyte that partitions into the film is based on the change in the attenuation of light passing through the guided wave substrate that accompanies an electrochemical reaction of the analyte induced by electromodulation. Threefold selectivity for a chosen analyte relative to other environmental components is obtained by the choice of coating material, the electromodulation potentials, and the wavelength for optical monitoring.

The sensor concept has been demonstrated with an indium tin oxide coated glass guided wave device that has been over-coated with the the selective film. The following charge-selective thin films have been evaluated: sol-gel derived PDMDAAC-SiO_2 composite (where PDMDAAC = poly(dimethyl diallylammonium chloride)), sol-gel derived Nafion-SiO_2 composite (where Nafion is a perfluorosulfonated ionomer), and poly(vinyl alcohol)-polyelectrolyte blend. Model analytes that have been used are $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Ru(bipy)_3^{2+}$ (where bipy = 2,2'–bipyridine), $Re(DMPE)_3^{1+}$ (where DMPE = 1,2-bis(dimethylphosphino)ethane), and MV^{2+} (methyl viologen dication). Performance characteristics such as selectivity, sensitivity, detection limit, response range, response time, and reversibility have been measured for these sensors. Improvement in detection limit by ensemble averaging a repetitive signal modulated by a potential step or potential scan excitation signal has been demonstrated. The effect of different waveforms for modulation on sensor performance has been investigated. Smaller sensors based on optical waveguides have been fabricated and their enhanced sensitivity demonstrated. A small portable sensor unit including a virtual interface, control electronics and optics has been developed. A procedure for the determination of ferrocyanide in Hanford waste tank simulant solution (U-Plant-2, prepared at PNNL) has been developed.

The development of a sensor for technetium in the TcO_4^- form that is applicable to characterizing and monitoring the Vadose Zone and associated subsurface water at the Hanford site began 6 months

ago. The key to adapting the generic sensor concept to detect TcO_4^- lies in the development of unique chemistry within the chemically selective film to provide a modulated optical response. This film is being developed so that TcO_4^- in the sample will partition into it by electrostatic attraction. Once TcO_4^- is loaded into the film, it is electrochemically converted into a Tc coordination compound that gives a strong optical signal associated with an electrochemical reduction/oxidation process. The magnitude of the absorbance change accompanying the electrochemical modulation of this coordination compound will quantitate the concentration of Tc within the film, which is proportional to the concentration of TcO_4^- in the sample. Research during the first 6 months has focused on studying the electrochemistry of perrhenate, ReO_4^-, which is being used as a surrogate for TcO_4^-, and evaluating suitable ligands to form the coordination compound in the sensing film. A variety of diphosphonate- and thiol-based ligands with previously demonstrated capability for coordinating with Tc have been evaluated.

30 presentations at scientific meetings have been made since the inception of the project. 14 original research articles have been published in scientific journals.

Planned Activities

The general development of the sensor concept and testing for ferrocyanide will be finished in the next 6 months. The ferrocyanide sensor is scheduled for testing on waste tank simulant at PNNL in April 2000. Results will be compared with a standard spectroscopic method developed by Bryan. The search for a good ligand and a good charged polymer for the sensing film for the pertechnetate sensor will continue for the next 6 months with the surrogate perrhenate. The best candidates will then be tested with pertechnetate at PNNL. Presentations at the following meetings will be made: Pittcon 2000 (5 by graduate students), spring ACS (1), ESEAC 2000 (1).

Information Access

Original research articles resulting from this project (11 of 14 are listed):

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 1. Demonstration of Concept with Ferricyanide, Y. Shi, A. F. Slaterbeck, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 69, 3679-3686 (1997).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 2. Demonstration of Selectivity in the Presence of Direct Interferents, Y. Shi, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 69(23), 4819-4827 (1997).

New Spectroelectrochemical Sensor, Y. Shi, A. F. Slaterbeck, S. Aryal, C. J. Seliskar, W. R. Heineman, T. H. Ridgway, J. H. Nevin, *SPIE,* 3258, 56-65 (1998).

New Chemically-Selective Optical Materials for Waveguide Sensors, L. Gao, Y. Shi, A. F. Slaterbeck, C. J. Seliskar, W. R. Heineman, *SPIE,* 3258, 66-74 (1998).

Evaluation of the Electrochemical Characteristics of a Poly(vinyl alcohol)/poly(acrylic acid) Polymer Blend, C. O. Dasenbrock, T. H. Ridgway, C. J. Seliskar, W. R. Heineman, *Electrochim. Acta*, 43(23), 3497-3502 (1998).

Electrochemical Behavior of Methyl Viologen at Graphite Electrodes Modified with Nafion Sol-Gel Composite, B. Barroso-Fernandez, M. T. Lee-Alvarez, C. J. Seliskar, W. R. Heineman, *Anal. Chim. Acta*, 370, 221-230 (1998).

Dual Analyte Spectroscopic Sensing in Sol-Gel Derived Polyelectrolyte-Silica Composite Thin Films, Y. Shi, C. J. Seliskar, W. R. Heineman, *Talanta,* 47, 1071-1076 (1998).

Voltammetry of $[Re(DMPE)_3]^+$ at Ionomer-Entrapped Composite-Modified Electrodes, Z. Hu, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 70, 5230-5236 (1998).

Tailoring Perfluorosulfonated Ionomer-Entrapped Sol-Gel-Derived Silica Nanocomposite for Spectroelectrochemical Sensing of $Re(DMPE)_3^+$, Z. Hu, A. Slaterbeck, C. J. Seliskar, T. H. Ridgway, W. R. Heineman, *Langmuir,* 15, 767-773 (1999).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 3. Effect of Signal Averaging on Limit of Detection, A.F. Slaterbeck, T.H. Ridgway, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 71, 1196-1203 (1999).

Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 4. Sensing with Poly(vinyl alcohol)-Polyelectrolyte Blend Modified Optically Transparent Electrodes, L.Gao, C. J. Seliskar, W. R. Heineman, *Anal. Chem.,* 71, 4061-4068 (1999).

Novel Analytical Techniques Based On an Enhanced Electron Attachment Process

Project ID: 55328

Lal A. Pinnaduwage, University of Tennessee

Michelle V. Buchanan, Oak Ridge National Laboratory
Gregory B. Hurst, Oak Ridge National Laboratory

Research Objective

The objective of this research program is to develop new analytical techniques based on the large cross sections associated with dissociative electron attachment to highly-excited molecular states. Such highly-excited states can be populated by using fixed frequency lasers or in glow discharges via excitation transfer from high-lying, metastable states of rare gases. It is anticipated that these studies will lead to negative-ion based analytical techniques for the detection of DNAPLs (dense non-aqueous phase liquids), VOCs (volatile organics) and other toxic compounds at DOE waste sites. We have made significant advances toward this goal as described below.

Research Progress and Implications

We have pursued the development of (i) laser based, and (ii) glow discharge based analytical techniques, and have conducted studies to elucidate the basic mechanisms and to move the project closer to field applications. We have illustrated that long lived core-excited high-Rydberg states can be produced using fixed frequency lasers (JP1, JP4, JP12) and glow discharges (JP2, JP3, JP13), and that efficient negative ion formation can be achieved using lasers (JP5,JP11) and glow discharges (JP6,JP8,JP10). Electron attachment mechanisms were clarified (JP5, JP7, JP9, JP12, JP14). We have built a solid foundation for the development of novel laser and glow discharge based analytical instruments.

Planned Activities

If the research grant is renewed, we plan to achieve the following goals:

1. Optimize laser-induced negative ion formation by incorporating an electron gun.
2. Collaborate with Comstock, Inc in Oak Ridge to build a portable laser based mass spectrometer that can function in both negative and positive ion modes.
3. Incorporate a quadrupole mass spectrometer to the plasma apparatus for mass analysis.
4. Build a novel electron capture detector based on the glow discharge excitation scheme.

Information Access

JP1. L. A. Pinnaduwage and Y. Zhu,"Long-Time Stability of Superexcited High Rydberg Molecular States", *Chem. Phys. Lett*. **277**, 147 (1997).

JP2. 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).

JP3. 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.

JP4. L. A. Pinnaduwage and Y. Zhu, "High Rydberg Fragment Formation via Core Dissociation of Superexcited Rydberg Molecules", *J. Chem. Phys*. **108**, 6633 (1998).

JP5. K. Nagesha and L. A. Pinnaduwage, "O^- Formation from O_2 via Rydberg-Rydberg Electron Transfer" *J. Chem. Phys.* **109**, 7124 (1998).
JP6. 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).
JP7. A. M. Mabel, S. H. Lin, and L. A. Pinnaduwage, "Potential Energy Surfaces of H_2^-", *Chem. Phys. Lett*. **285**, 114 (1998).
JP8. 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).
JP9. 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).
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**, 384-391 (1999).
JP11. L. A. Pinnaduwage, K. Nagesha, Y. Zhu, M. V. Buchanan, and G. B. Hurst, "Laser-Enhanced Negative Ion Mass Spectroscopy for Weakly-Electron-Attaching Species", *Int. J. Mass Spectrometry* **193**, 77-86 (1999).
JP12. K. Nagesha and L. A. Pinnaduwage, "Magnetic and Electric Field Induced Enhancements in Laser Induced Anion Formation", Chemical Physics Letters **312**, 19-27 (1999).
JP13. 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).
JP14. C. Tav and L. A. Pinnaduwage, "Enhanced Dissociative Electron Attachment to Laser-Excited Benzene", submitted to J. Chem. Phys. (1999).

Patent

L. A. Pinnaduwage, "A Novel Glow Discharge Process for Analytical Applications," Patent No. 5,896,196 (1999).

Microsensors for In-Situ Chemical, Physical, and Radiological Characterization of Mixed Waste

Project ID: 60197

Thomas G. Thundat, Oak Ridge National Laboratory

R.J. Warmack, Oak Ridge National Laboratory
G. M. Brown, Oak Ridge National Laboratory
R. Dabestani, Oak Ridge National Laboratory
P.F. Britt, Oak Ridge National Laboratory
P. V. Bonnesen, Oak Ridge National Laboratory

Research Objective

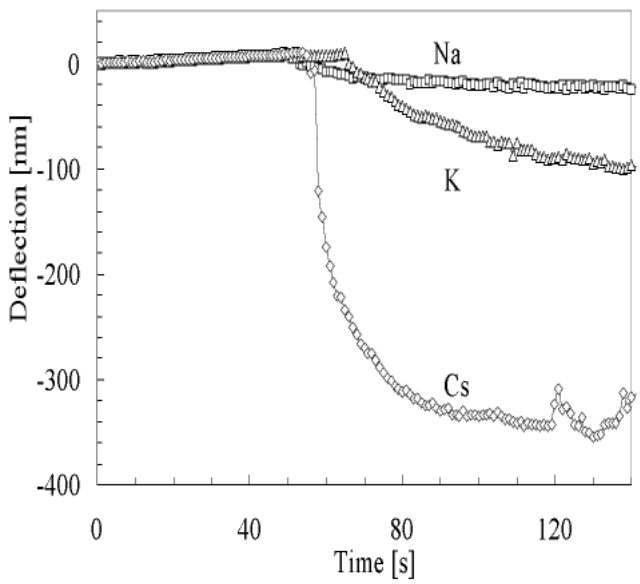
A widespread need exists for portable, real-time, in-situ chemical, physical, and radiological sensors in the characterization and monitoring of mixed waste, ground water, contaminated soil and process streams. A number of environmental monitoring scenarios could benefit from miniature, low-power instrumentation that provides multicomponent analysis and information in an autonomous fashion. For example characterization of ground water is important for plume containment and remediation efforts. Urgent need also exists for sensors for determination of location, chemical composition, and level of Dense Non-Aqueous Phase Liquids (DNAPLs).

The objective of this research program is to conduct the fundamental research to develop extremely sensitive and highly selective sensors for chemical, physical, and radiological characterization of mixed waste and ground water using microcantilever platform. The microcantilever sensors have sensitivity in the range of parts-per-trillion. These sensors will be of great value to DOE for the safe and cost-effective in situ, real-time characterization of contaminated sites. The ability to detect and measure specific chemicals and radionuclides in real-time using miniature and inexpensive sensing devices could result in considerable benefits with regard to both cost savings and safety issues. In addition, this approach can also lead to multi-element/multi target sensors using array approach. The selectivity of the sensor results from chemical modification of cantilevers using selective molecular recognition agents.

Research Progress and Implications

As of mid-third year great progress has been made toward demonstrating many chemical, physical, and radiological sensors with unprecedented sensitivity and selectivity. The demonstrated examples include detection of Cs ions with 10^{-12} M sensitivity in the presence of high concentrations of Na^+ and K^+ ions. To make the microcantilevers selective for Cs, the cantilevers were coated with cesium-selective ionophores (which have selectivities for cesium over sodium in the range of 20,000 to 50,000). We have used chemically modified 1,3-alternate 25,27-dialkoxy –26,28-calix[4]-benzo-crown-6 ionophores, for attachment to the microcantilever. The ionophores for cesium ion detection were synthetically modified with long-chain alkanethiols for attachment to a gold-coated microcantilever. The octyl chains were derivatized with terminal thiols for adsorption onto gold. In order to form a compact monolayer, a shorter chain amphiphile 1-decanethiol was co-absorbed onto the gold surface to fill the gaps present between the two alkyl thiol arms of the ion selective ionophores and the adjacent molecules.

The following figure shows the selective response of a modified cantilever for detection of Cs^+, K^+, and Na^+ ions.



Another great successful demonstration was detection of Cs ions in a tank waste simulant with high concentrations of sodium nitrate and NaOH (pH 14). In addition we have demonstrated selective and sensitive sensors for Na, K, and CrO_4. We have also developed extremely sensitive pH sensors with sensitivity of 10^{-3} pH units. Examples in chemical sensing include detection of benzene, toluene, and hydrogen. We have demonstrated a novel micromechanical detector for alpha particle detector using microcantilevers.

Planned Activities

During the remainder of this fiscal year, we will focus our attention on the development of modified cantilevers for characterization of selected inorganic species (Pb, Hg, Cr, and Sr) in ground water. Experiments are presently underway to evaluate and optimize microcantilever radiation detector for alpha particles.

Information Access

T. Thundat, E. Finot, H-F. Ji, R. Dabestani, P.F. Britt, P.V. Bonnesen, G.M. Brown, and R.J. Warmack, "Highly selective microcantilever sensor for Cs ion detection" Electro. Chem. Soc. Pro. 99-23, pp 314-319 (1999).

T. Thundat and L. Maya, "Monitoring chemical and physical changes on sub-nanogram quantities of platinum oxide" Surf. Sci. Lett . **430** L546 (1999).

H-F. Ji, E. Finot, R. Dabestani, T. Thundat, P.F. Britt, and G.M. Brown," Chem. Comm. (in press).

A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals

Project ID: 55205

Dr. Scott Goode, University of South Carolina

Research Objectives

Improved technologies are required by DOE for characterization and monitoring for site clean-up and waste processing applications. Especially needed are field deployable methods and devices of real-time monitoring to reduce dependency on laboratory analyses which are costly and time consuming. Improved sensors are needed for on-site analyses to provide real-time analytical capabilities for screening level and/or decision-quality data. Matrices of interest to the DOE are soils (or other solids), slurries, and aqueous and non-aqueous solutions.

Laser-induced breakdown spectroscopy (LIBS) is a useful method for determining the elemental composition of solids. This method has been recently reviewed and a number of different applications have been described. In the LIBS technique, a high-power pulsed laser is used to generate a plasma from the sample of interest. This phenomenon was first demonstrated in 1963 using a pulsed ruby laser. The elemental composition of the sample is accomplished by measuring the atomic emission from the atoms and ions in the plasma. There are many reports of the use of LIBS for measuring metals in solid substrates. There have also been LIBS investigations of aerosols, single particles, metals in solution including uranium, and even chlorinated species in solution. More recently, LIBS has been used for measuring Ba and Cr in soil using a fiber-optic cable. LIBS shows great potential for measuring metal contaminants in soils and on particles (e.g., stack emissions) based on their atomic emission in a laser-induced plasma. Another important application for this technique is the remote analysis of highly radioactive materials, such as the glasses produced by the Defense Waste Processing Facility. The use of fiber optics for both collection of the atomic emission and delivery of the laser to the sampling area could eliminate the need for sampling.

In this work we will study the time-evolution of the LIBS emission for different matrices to better understand how to optimize the signal. Also, we will investigate the use of fiber optics for laser delivery and signal collection, and the influence of the geometry of the fiber optic launch and collection probes to determine the effect on the signal-to-noise ratio (SNR). Finally, we will study the LIBS signal for different sample matrices as a function of excitation wavelength across a broad spectrum. A result of this study should be a determination of the optimal excitation and collection conditions and sampling times for metal contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for LIBS sampling.

Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites

Project ID: 54639

Dr. Joseph Wang, New Mexico State University

Chung-Chiun Liu, Case Western Reserve University
Khris B Olsen, Pacific Northwest National Laboratory

Research Objective

The goal of this program is to develop, optimize and deploy a silicon-based micromachined stripping analyzer for field monitoring trace levels of chromium and uranium. Such system will integrate the sample-handling steps and necessary chemical reactions (using a flow-injection operation) with the actual adsorptive stripping measurement on a small planar chip. Besides the drastic reduction in the size of the analytical system, such miniaturization should lead to increased speed, minimal reagent consumption and disposal, higher sensitivity and improved precision, and would thus revolutionize the way by which toxic metals are being monitored.

Research Progress and Implications

Two avenues have been explored over the past 2.5 years for achieving the overall goal of field monitoring of Cr and U, as well as of other toxic metals. These include a micromachined hand-held flow stripping analyzer and a remotely deployed submersible stripping probes. Both routes should allow testing of trace metals more rapidly and easily in a field setting.

Remotely deployable submersible sensors, capable of monitoring metal contaminants both in time and location are advantageous for environmental monitoring. Over the past year we expanded the scope of our remote monitoring capability by integrating a sample processing capability. Such coupling of the sample handling with the actual stripping detection on a cable platform represents a powerful and innovative approach for in-situ environmental analysis.

Our initial flow probe was designed for delivering internally the ligand and catalyst (DTPA-NO_3^-) essential for adsorptive-catalytic measurements of trace Cr (1). Such renewable-reagent sensor thus relies on delivery of the reagent solution, its complexation reaction with the Cr ion collected in a semi-permeable microdialysis sampling tube, and transport of the complex to the downstream detector. The resulting in-situ sensor has a detection limit of 0.1 ppb Cr, as well as good precision and stability (e.g, RSD of 6% at 25 ppb), with no carry-over (memory) effects (e.g., Fig. 1). A stable response was observed for both Cr (VI) and Cr(III) species.

Performing on-cable various sample manipulations was shown to offer additional advantages. For example, a 'built-in' acidification capability was employed for monitoring the total metal concentration (2). Such on-cable acidification of the collected samples offered an in-situ release (decomplexation) of metals bound to various ligands. This was documented for samples rich with NTA and EDTA. The released metals were detected by stripping potentiometry. The design of the flow probe is shown in Figure 2. The versatility of this submersible 'microlaboratory' was demonstrated also for circumventing in-situ common problems associated with stripping analysis (3). In particular a judicious choice of the internal solution was shown useful for addressing the formation of intermetallic compounds or overlapping signals. These were accomplished through an internal delivery of a third element or a masking agent, respectively.

Additional efforts in the direction of remote electrochemical sensors have led to the developments of useful probes for in-situ monitoring of trace mercury (4) and nitroaromatic explosives, such as TNT (5), in connection to potentiometric stripping and square-wave voltammetric detection, respectively.

We have designed and fabricated different configurations of the micromachined metal analyzer (e.g., Figure 3). Such hand-held flow systems integrate the sample processing step with the stripping detector. We used an arrangement of functional modules (inch^2), stacked on top of each other, to form the miniaturized flow system. These include the sample and ligand reservoirs, micropumps, mixer, reaction coil, flow detector, and electronic control. This represents the smallest metal analyzer ever reported. Such dramatic scaling down has been very challenging (from the microfabrication angle) and led to various challenges or obstacles (e.g., solution leaks, pump stability, peeling off of electrode layers), and hence to delays in our planned Fall 99 delivery. We are working closely with our new subcontractor (Case Western Reserve University) for addressing these challenges, and have

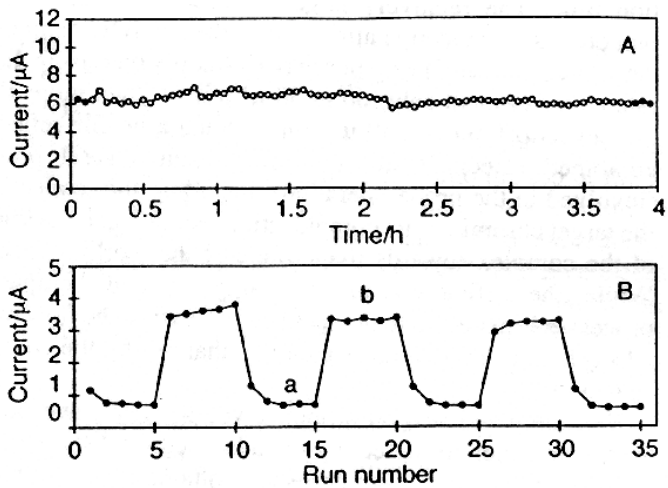


Figure 1. Performance of the in-situ probe for monitoring trace Cr: (A) Stability and (B) carry-over experiments. (A) Repetitive measurements of 25 ppb Cr(VI); response to alternate exposures to low (5ppb) and high (25ppb) Cr(VI) levels. Preconcentration time, 30 sec. (From ref. 1.)

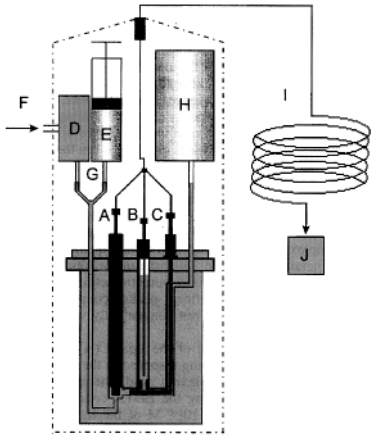


Figure 2. Schematic of the acid-delivered remote total-metal sensor. (From ref. 2.)

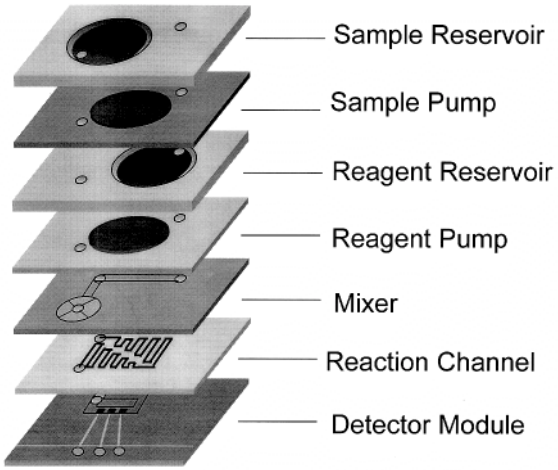


Figure 3. View of the stacked micromachined flow analyzer for adsorptive stripping monitoring of metal contaminants. (From ref. 6.)

requested a 1-year no-cost extension for completing the planned evaluation of the microanalyzer and demonstration of its attractive analytical/field performance.

Planned Activities

During the 99 summer, and in FY2000, we expect to expand the on-cable sample-manipulations capability, by integrating more challenging processes, in a so called 'Lab-on-Cable'. Such submersible 'microlaboratory' will perform all the necessary sample pretreatment steps, should have a major impact upon the monitoring of priority pollutants. We have recently completed the design of this device, and planning to characterize, optimize, and test it thoroughly during the coming 15 months.

We are also planning to receive from our subcontract the final design of the micromachined flow metal analyzer early this summer, and expect to assess and optimize its performance during the Fall 99 period, and extensively test and demonstrate its unique capabilities in lab and field settings during the FY 2000 season.

List of Publications (3rd year Funding Period)

1."Flow Probe for *in-situ* Electrochemical Monitoring of Trace Chromium", J. Wang, J. Lu, B. Tian, D. MacDonald, and K. Olsen, Analyst, 124(1999)349.
2. "Electrochemical Flow Sensor for in-situ Monitoring of Total Metal Concentrations", J. Wang, B. Tian, J. Lu, Anal. Communications, 35(1998)241.
3. "In-situ Flow Probe for Improving the Performance of Electrochemical Stripping Analysis", J. Wang, J. Lu, and M. Augelli, Fres. J. Anal. Chem., 364(1999)28.
4. "Remote Electrochemical Sensor for Monitoring Trace Mercury", J. Wang, B. Tian, J. Lu, and D. MacDonald, Electroanalysis 10(1998)399.
5. "Remote Sensor for Monitoring TNT in Natural Waters", J. Wang, R. Bhada, J. Lu, and D. MacDonald, Anal. Chim. Acta, 361(1998)85.
6. "Stripping Analysis into the 21st century: Faster, Smaller, Simpler, and Better", J. Wang, B. Tian, J. Lu, C. Yarnitsky, K. Olsen, and W. Bennet, Anal. Chim. Acta, 385(1999)429.

Radionuclide Sensors for Water Monitoring

Project ID: 70179

Dr. Jay W. Grate, Pacific Northwest National Laboratory

Dr. Oleg B. Egorov, Pacific Northwest National Laboratory
Dr. Timothy A. DeVol, Clemson University

Research Objective

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

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

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

Research Progress and Implications

This report summarizes work for the first 6 months of a 3-year program. The initial ongoing effort is directed at the investigation of the preconcentration column sensor concepts, development and characterization of the selective scintillating microspheres (SSMs), and development of the new scintillation detection systems. The preconcentrating minicolumn radionuclide sensor is based on the use of dual-functionality bead materials. These materials are designed to incorporate both selective separation chemistry for analyte preconcentration and localization within the detector, and scintillating fluors, so that radioactivity of retained species can be transduced to a measurable light output. To date we have achieved progress in SSM materials prepared by co-immobilization of selective organic extractants and scintillating fluors within inert polymeric beads. Scintillating microspheres selective for Tc, Sr, and actinides were prepared. Using pertechnetate-selective scintillating beads, we have demonstrated the feasibility of a renewable preconcentrating column sensor concept in successful application toward ^{99}Tc determination in contaminated ground water samples from the Hanford site. To avoid sensor material degradation during the regeneration step, the sensor column was renewed via fluidic bead replacement. Using a 50-mL sample volume and 30-minute counting time, the detection limit for ^{99}Tc was 0.37 dpm/mL (9.8 pg/mL). This detection limit is below the maximum permissible drinking water level of 2 dpm/mL. This study is a subject of a recent publication.(1)

In addition, research has commenced on a combined extraction chromatographic and scintillation resin in a solid support for on-line and off-line monitoring of radiostrontium in aqueous solutions.

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

Actinide SSMs have been developed and characterized to determine feasibility for sequential elution of radioactive species. Tests have indicated that although sequential separation is feasible, available energy resolution information is limited. In addition to the limited energy resolution of the SSM, variable quench associated with different chemical eluants is significant. The absolute detection efficiency of the actinide SSM depends on alpha energy and ranges from ~80% to nearly 100%.(2) Development of a photodiode-based scintillating microsphere detection system continues. The photodiode-based system offers several advantages over commercially available photomultiplier-based systems to include: better pulse shape discrimination capability, higher sensitivity at certain scintillation wavelengths, compactness and reduced power requirements.

Planned Activities

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

Information Access

(1) O.B. Egorov; S.K. Fiskum; M.J. O'Hara; J.W. Grate; "Radionuclide Sensors Based on Chemically Selective Scintillating Microspheres: Renewable Column Sensor for Analysis of ^{99}Tc in Water", *Anal. Chem.* 1999, *71*, 5420-5429.

(2) T.A. DeVol, J.E. Roane, J.M. Williamson, J.M Duffey and J.T. Harvey; "Development of Scintillating Extraction Media for Separation and Measurement of Charged-Particle Emitting Radionuclides in Aqueous Solutions," submitted for publication in *Radioactivity and Radiochemistry*.

(3) T. DeVol, O.B. Egorov, J.E. Roane, A. Paulenova, and J.W. Grate; "Extractive Scintillating Microspheres for ^{99}Tc Quantification in Aqueous Solutions," submitted for presentation to Fifth International Conference on Methods and Application of Radioanalytical Chemistry, Kailua-Kona, HI, April 9-14, 2000.

(4) J.M. Duffey, A. Paulenova, and T.A. DeVol, "Combined Extraction Chromatography and Scintillation Detection for On-line and Off-line Monitoring of Strontium in Aqueous Solutions," submitted for presentation to Fifth International Conference on Methods and Application of Radioanalytical Chemistry, Kailua-Kona, HI, April 9-14, 2000.

Construction of Bending Magnet Beamline at the APS for Environmental Studies

Project ID: 54800

Dr. Edward A. Stern, University of Washington

Research Objective

To help satisfy the growing need for synchrotron radiation based environmental research, it is proposed to carry out the design and construction of a bending magnet (BM) beamline at the Advanced Photon Source (APS) by the Pacific Northwest Consortium-Collaborative Access Team (PNC-CAT). The line will be optimized for various forms of x-ray absorption spectroscopies (XAS). Environmental and cleanup issues are a major focus of the fundamental research to be performed on the BM beamline. The beamline will share the PNC-CAT experimental facilities to be fabricated for the neighboring Undulator A Insertion Device beamline to utilize the experimental techniques of x-ray absorption spectroscopy for both bulk and surface studies, with spatial and time resolution and elemental imaging, on toxic and radioactive samples. These capabilities have been cited in a recent DOE workshop report as most desirable for future environmental research.

Synchrotron radiation studies of materials at the molecular scale can make important contributions to the understanding of the basic science issues underlying environmental cleanup efforts. A recent DOE workshop report "Molecular Environmental Science: Speciation, Reactivity, and Mobility of Environmental Contaminants" (July 5-8, 1995) emphasizes the important role to be played by synchrotron techniques, especially in the hard x-ray range. This view is confirmed by the increasing numbers of environmental programs which are employing synchrotron techniques, and the report also concludes that the available beamtime for such experiments is likely to be saturated in the near future. It is equally important that the beamtime be accompanied by the appropriate support for environmental studies, such as the capabilities for handling radioactive samples. To address these issues the Pacific Northwest Consortium-Collaborative Access Team (PNC-CAT) is proposing to build the optics and beam transport of a bending magnet beamline to deliver x-rays to an experimental enclosure. The beamline will be located at sector 20 of the Advanced Photon Source (APS), and will share important environmental support facilities with an insertion device beamline already under construction.

The PNC-CAT is a consortium of researchers from Universities in Washington State, Canada, and the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. The PNC-CAT was formed to develop a sector at the Advanced Photon Source (APS), a third-generation synchrotron radiation x-ray source under construction at Argonne National Laboratory. This source will be completed in 1996-1997, and its distinguishing feature will be the use of insertion devices such as undulators which increase source brightness by orders of magnitude over previous generation synchrotrons. The PNC-CAT will employ this source brilliance to develop a unique x-ray microbeam of unprecedented flux density with beam size and resolution down to ~0.1 micron, and tunable over the range 4-25 keV for a variety of research projects. Equipped with an x-ray microprobe, advanced fluorescence detectors, radioactive sample facilities, and surface scattering and XAFS equipment, the PNC-CAT beamlines provide unique facilities for basic research into environmental problems.

The University of Washington (UW) has recently recognized its special responsibility because of its geographic location, to help in solving the clean-up problems at the badly contaminated Hanford, Washington, site. The University Administration has been encouraging Faculty involvement in this activity (see Letter in Appendix A). In particular, as stated in the Letter, "The University of Washington will match all awards received through the EMSP program at the level of 10%." The facilities in this research will not only give unique capabilities to investigate the research problems proposed here,

but also will be of use to the programs of other researchers, including collaboration with researchers from UW and PNNL as outlined in Section D. For example, a number of ongoing Environmental Management (EM) problems will be addressed by the basic research planned for the beamlines. These include:

- Improved waste processing and separation technologies.
- Alternative waste forms capable of better handling of problematic species such as Ti or phosphates.
- Verification of modeling for the transport of contaminants under geologic conditions.
- Chemical speciation of tank wastes.
- Atomic scale structure of active sites in metallo-enzymes proposed for bio-catalytic reduction of actinides, metal contaminants and chlorinated hydrocarbons.
- Adsorption and catalytic interactions at mineral surfaces.
- Radiation induced structural changes in waste forms.
- Improved sensors for monitoring contaminants.

The estimated number of key personnel who will be utilizing this instrumentation consists of the following: senior personnel, 37; post-docs, 10; graduate students, 20; and undergraduates, 5. The members of the PNC-CAT cover a broad spectrum of interest. All are interested in the fundamental properties of "materials" but differ in the materials being investigated and the areas of application of this basic knowledge. The unifying element is the PNC-CAT and the experimental capabilities that its facilities will present. As has been the experience at other synchrotron sources, the PNC-CAT is expected to catalyze interactions between governmental and industrial researchers, graduate students, professors and post-docs from different fields which would not have occurred otherwise.

Monitoring Genetic and Metabolic Potential for In-Situ Bioremediation: Mass Spectrometry

Project ID: 55108

Michelle V. Buchanan, Oak Ridge National Laboratory

Phillip F. Britt, Oak Ridge National Laboratory
Mitchel J. Doktycz, Oak Ridge National Laboratory
Gregory B. Hurst, Oak Ridge National Laboratory
Mary E. Lidstrom, University of Washington

Research Objective

A number of DOE sites are contaminated with dense non-aqueous phase liquids (DNAPLs) such as carbon tetrachloride and trichloroethylene. At many of these sites, microbial bioremediation is an attractive strategy for cleanup, since it has the potential to degrade DNAPLs *in situ*. A rapid screening method to determine the broad range potential of a site's microbial population for contaminant degradation would greatly facilitate assessment for *in situ* bioremediation, as well as for monitoring ongoing bioremediation treatment. Current laboratory-based treatability methods are cumbersome and expensive. In this project, we are developing methods based on matrix-assisted laser desorption/ ionization mass spectrometry (MALDI-MS) for rapid and accurate detection of polymerase chain reaction (PCR) products from microbial genes involved in biodegradation of pollutants. PCR primers are being developed to amplify DNA sequences that are amenable to MALDI-MS detection. This work will lay the foundation for development of a field-portable MS-based technique for rapid on site assessment and monitoring of bioremediation processes.

Research Progress and Implications

This report summarizes work at the end of a 3-year project, during which we have demonstrated improved MALDI-MS detection of DNA signatures relevant to bacterial bioremediation.

A model system for interfacing PCR amplification with MALDI-MS detection is based on the *pmoA* gene for the active site subunit of particulate methane monooxygenase, a bacterial enzyme that can oxidize trichloroethylene. Andria Costello and Ann Auman, two graduate students in Prof. Lidstrom's laboratory, have developed molecular techniques for analyzing natural populations of methanotrophic bacteria, which are important for *in situ* bioremediation of halogenated solvents such as trichloroethylene, dichloroethylene and vinyl chloride. A DNA sequence database has been developed for methanotrophs in Lake Washington sediment, a habitat studied in detail by the Lidstrom laboratory. This database has been used to design specific PCR primers and hybridization probes that will detect the entire range of these diagnostic genes in known methanotrophs. These molecular tools have been used to analyze the natural populations of methanotrophs in Lake Washington sediments by conventional hybridization techniques. For MALDI-MS detection, PCR primer pairs were designed to amplify relatively short segments (99 bases and 56 bases) of *pmoA* in Type I and Type II methanotrophs.

To determine the range of conditions over which the combined PCR amplification, purification, and MALDI detection methodology is useable, we have varied amounts and types of bacterial DNA added initially to the PCR. MALDI signal can be detected from a PCR preparation that uses as little as 10^5 -10^6 target molecules. The effects of "interfering" DNA from the diverse microbial population found in subsurface environments were explored by performing PCR on mixtures of genomic DNA

from the methanotroph *Methylosinus trichosporium* OB3b and *E. coli*. In this initial study, the effect of the "interference" DNA was negligible.

A rapid reverse-phase purification of bacterial PCR products allows MALDI-MS detection from a fraction of one 25-microliter reaction. At this level of sensitivity, MALDI-MS is competitive with conventional methods for detecting PCR products in the <100 bp size range, and methodology improvements should allow larger products to be analyzed. Recovery of the purification is 60% to 75% for PCR products of 50 to 200 bases. We have adapted the purification to a microtiter format for parallel treatment of 96 samples in about 10 minutes.

An important aspect of automated, high throughput MALDI analysis is improving the homogeneity of the dried MALDI matrix/PCR mixture to allow useful signal to be obtained by aiming the MALDI laser anywhere on the spot. Polymeric substrates are proving useful in this regard. A combination of fluorescence microscopy for visualizing the distribution of DNA in the MALDI sample and MALDI measurements of the same spots guides the optimization of the substrate development work. While typical DNA samples for MALDI prepared on a bare metal substrate have a dried "rim" of DNA-doped matrix crystals, samples prepared on polymeric substrates tend to be more evenly distributed across the entire area originally wetted by the sample solution droplet. The mechanism appears to involve increased viscosity in the drying droplet due to partial re-dissolution of the polymer substrate, as well as partitioning of either the DNA or the matrix between the solvent and the remaining polymeric substrate.

Planned Activities

A proposal is being prepared for continuation of this project, which was funded through FY 1999, with a no-cost extension through March 2000.

Information Access

G.B. Hurst, K. Weaver, M.V. Buchanan and M.J. Doktycz, "Analysis of PCR products using delayed-extraction MALDI-TOF," Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs CA, June 1-5, 1997, p. 843.

G. B. Hurst, K. Weaver, and M.V. Buchanan, "Improved Mass Spectrometric Resolution for PCR Product Size Measurement," presented at The Sixth Department of Energy Contractor and Grantee Workshop of the Human Genome Program, Santa Fe, NM, November 9-13, 1997.

G.B. Hurst, K. Weaver, M.J. Doktycz, M.V. Buchanan, A.M. Costello, and M.E. Lidstrom, "MALDI-TOF Analysis of Polymerase Chain Reaction Products from Methanotrophic Bacteria," *Anal. Chem.* 1998, *70*, 2693-2698.

G.B. Hurst, K. Weaver, M.J. Doktycz, M.V. Buchanan, A. Costello, and M.E. Lidstrom, "Identification of Methanotrophic Bacteria Using the Polymerase Chain Reaction with MALDI-TOF Detection," Proceedings of the 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando FL, May 31-June 4, 1998, p. 1202.

K. Weaver, M.J. Doktycz, P.F. Britt, G.B. Hurst, and M.V. Buchanan, "96-Well Microtiter-Format Purification of DNA for MALDI-TOF Analysis," Proceedings of the 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando FL, May 31-June 4, 1998, p. 60.

M.V. Buchanan, G.B. Hurst, M.J. Doktycz, P.F. Britt, K. Weaver, M.E. Lidstrom and A.J. Costello, "Monitoring Genetic and Metabolic Potential for in situ Bioremediation: Mass Spectrometry," Poster presentation at the DOE Environmental Management Science Program Workshop, Chicago, Ill., July 27-30, 1998.

G.B. Hurst, Y. Kim, K. Weaver and M.V. Buchanan, "PCR Product Size Measurement using MALDI Mass Spectrometry," Poster presentation at the 7th DOE Human Genome Contractor-Grantee Workshop, Oakland, California, January 12-16, 1999.

Y. Kim, G.B. Hurst, M.J. Doktycz and M.V. Buchanan, "Improved Spot Homogeneity for DNA MALDI Matrices," to be presented at the 47th ASMS Conference on Mass Spectrometry and Allied Topics, Dallas TX, June 13-18, 1999.

Rapid Mass Spectrometric DNA Diagnostics for Assessing Microbial Community Activity During Bioremediation

Project ID: 54698

Dr. W. Henry Benner, Lawrence Berkeley National Laboratory

Research Objective

The use of DNA-based procedures for the detection of biodegrading organisms or genes that code for pollutant-degrading enzymes constitutes a critical technology for following biochemical transformation and substantiating the impact of bioremediation. In previous studies, DNA-based technology has been demonstrated to be a sensitive technique for tracking micro-organism activity at the molecular level. These procedures can be tuned to identify groups of organisms, specific organisms, and to detect signals that measure microbial community activity. This proposal describes the evaluation of a monitoring strategy that relies on the combined use of DNA diagnostics with mass spectrometry as the detection scheme. The intent of this work is a two-fold evaluation of: 1) the feasibility of replacing the use of gel separations for identifying polymerase chain reaction (PCR) products with a rapid and automatable form of electrospray mass spectrometry and 2) the use of matrix-assisted-laser-desorption-ionization mass spectrometry (MALDI-MS) as a tool to score oligonucleotide ligation assays (OLA).

Mass spectrometry is an attractive detection alternative for PCR and OLA procedures because it is a sensitive analytical technique capable of providing high sample throughput performance and the introduction of samples into a mass spectrometer is automatable. Mass spectra are generated rapidly, in the order of minutes, thus eliminating a time bottleneck caused by time-consuming gel electrophoresis separations. The adaptation of OLA for mass spectrometric analysis will cut costs by eliminating expensive reagents. The techniques are automatable which translates into a decreased human error rate when numerous samples are analyzed as a component of large scale bioremediation studies. The successful conclusion of the work will be the development of a mass spectrometry capability for sizing PCR products and scoring OLA tests in formats that provide high throughput and automation for bioremediation studies.

Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes

Project ID: 54893

Gregory R. Choppin, Florida State University

Dhanpat Rai, Pacific Northwest National Laboratory

Research Objective

Plutonium contamination is a major problem at many DOE sites. This project seeks to provide fundamental data and models for predicting plutonium speciation and environmental behavior that will allow evaluation of the many processes proposed for remediation of plutonium-containing DOE wastes. Basic to this prediction are 1) the complete fundamental data on aqueous complexation, solubility reactions, and geochemical conditions under which different plutonium oxidation states transform from one to another, and 2) a model containing this fundamental data that can predict site-specific reactions. We propose to summarize existing data and develop additional fundamental data to measure the oxidation state (or states) in a variety of solid/solution systems in the presence and absence of chemicals likely to be present in DOE wastes and which can promote redox transformations and complexation reactions. Specifically, we will 1) develop methodology to determine complexation constants of Pu(IV) with strongly complexing ligands, 2) determine stability constants of Pu(IV) with strong complexants such as EDTA, 3) determine the geochemical conditions under which different reductants (e.g., Fe(0), Fe^{2+}, H_2O_2) can reduce Pu(VI) to Pu(III)/Pu(IV) and oxidants (e.g., MnO_2 and radiolytic products) that can oxidize Pu(IV) to Pu(V)/Pu(VI), and 4) summarize fundamental Pu data for use in a model for predicting Pu behavior under different geologic conditions.

Research Progress and Implications

This report summarizes the research through last year of a 3-year project. To obtain reliable values of Pu(IV)-EDTA complexes applicable to a wide range in environmental conditions, we conducted studies on the solubility of PuO_2(am), the solubility product of which is reasonably well known, at 1) 0.001 or 0.0001 M total EDTA concentrations and pH values ranging from 1 to 13.5 and 2) pH values of approximately 9 and EDTA concentrations ranging from 0.00001 and 0.093 M. The aqueous Pu oxidation states of the complexed species were determined by x-ray absorption near edge spectroscopy and solvent extraction and were used to quantify the Pu(IV)-EDTA species. The comparison of our experimental solubility with the predictions based on literature data showed that the predicted concentrations depended on the pH but were orders of magnitude lower (e.g., at pH 8, the difference is approximately six orders of magnitude), indicating that the existing models were not adequate to represent complexation behavior of Pu(IV) with EDTA at pH values >4. The data were interpreted using the Pitzer ion-interaction model that is applicable to dilute as well as concentrated electrolytes. Our model was developed based on the solubility of PuO_2(am) at 0.0001 M EDTA concentrations and as a function of pH. This model was validated against the data in 0.001 M as a function of pH and the data at pH value of 9 and as a function of EDTA concentrations. The log K^0 values for the formation of $Pu(OH)_xEDTA^{x-}$ according to the generalized reaction

$$Pu^{4+} + xOH^- + EDTA^{4-} = Pu(OH)_xEDTA^{-x}$$

were determined to be 36.39, 44.74, and 49.64 for x = 1, 2, and 3, respectively. These different complexed species, as expected, are dominant in different pH regions.

Obtaining reliable thermodynamic data for Pu(V) is difficult because of its redox and/or disproportionation reactions in most aqueous systems. Thus, very limited data are available for this oxidation state. Therefore, it is of interest to determine whether thermodynamic data for Np(V), expected to be a good analog for Pu(V), can be used to predict Pu(V) behavior. The known stability of Pu(V) in PuO_2(am) suspensions in slightly acidic to near neutral conditions was used to study the solubility of PuO_2(am) in 0.4 and 4.0 M NaCl or $NaClO_4$ solutions ranging in pc_{H+} values from 4 to 9 as a function of time. The close agreement between the observed solubility and the predicted solubility using Pitzer ion-interaction parameters of Np(V) with Cl^- or ClO_4^- indicates that Pu(V), as expected, behaves in an analogous fashion to Np(V) and confirms the value of using Np(V) data to model Pu(V) behavior.

Although Pu(V)/Pu(VI) may be the dominant oxidation state in some specific conditions (e.g., ocean waters, laboratory experiments in aerobic water), there are many reductants in many geologic environments that would reduce the plutonyl species to the tri- or tetravalent states. Therefore, the reduction of PuO_2^+ was measured and showed inverse dependence on the H^+ concentration with a half-life for reduction 10^{-10} M Pu(V) in 10^{-3} M H_2O_2 of about 8 days. (H_2O_2 is a product of radiolysis of water.) To determine the kinetics of oxidation of Pu(IV) to PuO_2(V) and/or PuO_2(VI), studies on the effects of MnO_2 and NaOC1 were also conducted. The data showed Pu(IV) is readily oxidized to PuO_2(V) or PuO_2(VI) by these oxidants. Rate expressions are being developed to allow predictions of the redox kinetics as a function of pH and redox reagents.

Plutonium Speciation, Solubilization, and Migration in Soils

Project ID: 59996

Mary Neu, Los Alamos National Laboratory

Wolfgang Runde, Los Alamos National Laboratory
Richard G. Haire, Oak Ridge National Laboratory

Research Objective

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years. To properly control Pu migration in soils within Federal sites and onto public lands, better evaluate the public risk, and design effective remediation strategies, a fundamental understanding of Pu speciation and environmental transport is needed. The key scientific goals of this project are: to determine Pu concentrations and speciation at a contaminated DOE site; to study the formation, stability, and structural and spectroscopic features of environmentally relevant Pu species; to determine the mechanism(s) of interaction between Pu and Mn/Fe minerals and the potential release of Pu via redox cycling; and to model the environmental behavior of plutonium. Our long-term goal is to use characterization, thermodynamic, mineral interaction, and mobility data to develop better models of radionuclide transport and risk assessment, and to enable the development of science-based decontamination stategies.

This research will fill important gaps between basic actinide science and the problems impeding site clean-up, plutonium disposition, and accurate risk assesment. Information gained will allow for the development of technologies and clean-up approaches targeting particular plutonium contaminants and improved assessment of risks associated with actinide migration, site remediation, and decontamination. By combining very specific study of plutonium at the Rocky Flats Environmental Technology Site (RFETS), a well-characterized contaminated site, with laboratory studies on the most important plutonium and mineral component systems, we will provide essential knowdege of contaminant characteristics and distinguish critical geochemical processes and mechanisms.

Research Progress and Implications

This report summarizes work performed in the first 5 months of the 3rd year of a 3-year project. In the first two years we focused on 1) characterizing Pu in contaminated samples from the RFETS, 2) fundamental stability and migration studies of Pu(IV) colloids, 3) fundamental studies of An(IV) carbonates, and 4) thermodynamic database development and geochemical modeling (summarized in progress report 6/15/99). This fiscal year our focus is on 1) Pu-Mn phase interactions, 2) fundamental studies of $Pu(OH)_x(CO_3)_y^{4-x-2y}$ species, 3) colloid migration and 4) site-specific geochemical modeling.

From site remediation and site closure perspectives, our most important results are the first direct speciation and distribution analyses of Pu in samples from a contaminated site. Using a combination of techniques, we found that Pu in soil samples from the 903 pad area at RFETS is dispersed on micro- and macroscopic scales (and not locally concentrated or associated preferentially with any other element) and is Pu(IV) with spectroscopic features most consistent with PuO_2. These research results are very powerful for explaining very limited observed mobility of Pu, predicting future behavior, and evaluating/revising remediation, closure, and monitoring plans.

We compiled and evaluated available Pu thermodynamic data and removed inconsistencies to obtain an updated, defensible database for modeling. Accurate thermodynamic data are key to reliably

model the geochemistry of plutonium. Despite numerous reviews of thermodynamic data for Pu species, few databases contain the most recent data provided in the literature. We are now poised to use this database and site conditions to predict Pu speciation and resultant mobility.

We have prepared and extensively characterized manganese phases and performed a number of Pu sorption and coprecipitation experiments. Sorption kinetics, oxidation state changes, speciation as a function of loading, and total binding were all studied for a number of Pu species.

Planned Activities

Confirming our thermodynamic calculations (and predictions in the literature), we identified plutonium to be in the +IV state in the RFETS soil samples investigated. Potential release and dissolution scenarios include the formation of the $Pu(OH)_4(aq)$ solution species. The carbonate content of ground- or surface waters will affect the speciation and dictate the formation of mixed Pu(IV) hydroxocarbonato species, $Pu(OH)_x(CO_3)_y^{4-x-2y}$. These species have much higher stabilities and increase the solubility of PuO_2 by orders of magnitude compared to $Pu(OH)_4(aq)$. We will synthesize the ternary species, obtain characteristic optical spectra, and determine their stability. We have prepared and characterized the limiting carbonate in this series, $Pu(CO_3)_5^{6-}$, as well as the U(IV) and Np(IV) analogs, and are now in a position to identify the other Pu(IV) solution species. The stability constants obtained will be used to evaluate species potential formation and importance given conditions at specific contaminated sites.

We will use our Pu thermodynamic database to calculate the speciation of Pu(IV) under RFETS conditions and to define stability ranges for Pu(IV) species that may control the release of Pu from its characterized source PuO_2. Detailed Pu-Mn interactions and colloid migration studies will also be continued.

DNAPL Surface Chemistry: Its Impact on DNAPL Distribution in the Vadose Zone and its Manipulation to Enhance Remediation

Project ID: 70035

Dr. Susan E. Powers, Clarkson University

Dr. Stefan Grimberg, Clarkson University
Dr. Miles E. Denham, Westinghouse Savannah River Company
Dr. Michal Borkovec, Clarkson University

Research Objectives

The remediation of DNAPLs in subsurface environments is often limited by the heterogeneous distribution of the organic fluid. The fraction of DNAPL that is in the high conductivity regions of the subsurface can often be recovered relatively easily, although DNAPL in lower conductivity regions is much more difficult to extract, either through direct pumping or remediation measures based on interface mass transfer. The distribution of DNAPL within the vadose zone is affected by a complex interplay of heterogeneities in the porous matrix and the interfacial properties defining the interactions among all fluid and solid phases. These complex interactions are needed to understand the current distribution of DNAPL in the subsurface and to plan effective remedial strategies. Results of this effort could potentially be used to increase the accessibility and, therefore, the recovery of DNAPL during vapor extraction or other vadose zone remediation efforts.

The primary hypothesis of this work is that surface-active chemicals and/or microorganisms present in the unsaturated zone can significantly alter the interfacial phenomena governing the migration of DNAPLs, thereby affecting the accessibility of a DNAPL during remediation efforts. The surface-active materials are present in complex NAPL mixtures and are produced through microbial metabolic processes. The overall goal of this proposed research is to understand the role of and changes in interfacial phenomena on the accessibility of DNAPL in the vadose zone.

Research Progress and Implications

A multi-task approach involving experimental measurements at both laboratory and field scales has been designed to meet the objectives of this research. Materials for this research have been chosen to be applicable to vadose zone contamination problems at the Savannah River site (SRS). Initial stages of the research are focusing on well-characterized materials with a shift to site-specific media as the processes are understood. This research offers a unique opportunity to develop our fundamental understanding of the fate of DNAPLs in the vadose zone through both laboratory scale testing and evaluation of field samples collected at SRS. The fieldwork provides a detailed assessment of the distribution of DNAPL in the subsurface as a function of microbial populations, mineral characterization, and heterogeneous grain size distribution. Concurrent laboratory testing provides an understanding of the fundamental mechanisms governing these distributions.

With research activities beginning September 15, 1999, only preliminary progress has been made by March 1, 2000. Most significantly, fieldwork for the first year has been planned and completed. In addition, progress has been made on the design and construction of laboratory apparatus for multiphase flow experiments.

Two soil borings at each of two sites at SRS have been drilled and sampled. These sites were chosen based on differences in the NAPL composition, aqueous geochemistry, and geological strata. At one site, spent solvent (PCE/TCE) was co-disposed with water with a wide range of pH values.

NAPL at this site is generally found in lower permeability zones in the unsaturated zone with a pool suspected in the saturated zone above a green clay unit. NAPL at the second site was not co-disposed with acidic or basic waters. Contamination at this site is found in a clay unit at much shallower depths. Split spoon samples were collected from each of these borings over the depths that were expected to be most contaminated. Samples are presently being analyzed for total bacteriological counts (Acridine Orange Direct Counts), total organic contamination (gas chromatography headspace analysis), grain size and mineralogy distributions, and identification of TCE as well as PCE degrading microorganisms. Soil samples were collected under both aerobic and anaerobic sampling conditions. Preliminary analysis supports the expectation that microbial counts are closely correlated with NAPL contamination levels.

The laboratory component of this research has been limited primarily to method development and verification at this point in time. Analytical methods to support the field sampling have been taught and tested for quality control. Prototypes for the micromodels, which will be used for multiphase flow experiments, have been fabricated and are currently being improved to ensure the observed multiphase flow is not dominated by experimental artifacts.

Planned Activities

A three-pronged approach is planned for the next year of this project. These concurrent activities include:

1. Continued analysis and interpretation of field results.
2. Identification of conditions that lead to alteration of interfacial properties and, therefore, capillary flow. This includes consideration of variable NAPL composition, aqueous geochemistry (pH), microbial strains, microbial growth conditions. Adhesion and interfacial tension will be used as preliminary screening properties.
3. Begin analysis of the implications of altered interfacial properties on multiphase flow behavior in micromodels and capillary pressure-relative permeability columns.

Information Access

None available yet.

Transuranic Interfacial Reaction Studies on Manganese Oxide Hydroxide Mineral Surfaces

Project ID: 70176

Professor Heino Nitsche, Lawrence Berkeley National Laboratory

Dr. Jeffrey Serne, Pacific Northwest National Laboratory
Dr. David K. Shuh, Lawrence Berkeley National Laboratory
Dr. Glenn A. Waychunas, Lawrence Berkeley National Laboratory

Research Objective

The objective of this project is to provide fundamental knowledge on the interfacial reactions of neptunium and plutonium with manganese oxide and hydroxide mineral surfaces. This information is relevant to the transport of transuranic radionuclide (TRU) contaminants in the vadose zone. Several DOE sites have been contaminated by TRU discharges as a result of weapons activities. Manganese oxides, present as minor phases in the vadose zone, may preferentially sequester TRU and transition metals over iron oxide/hydroxide minerals present in much larger amounts.[1,2] Neptunium and plutonium are highly toxic and potentially mobile in the vadose zone. Transport depends on the physical and chemical reactions between the neptunium or plutonium and the geological material. The data obtained from this project will be used for reactive transport modeling of TRU in the vadose zone, where the processes determining the retardation, immobilization, mobilization and permanence of TRU are poorly understood. Transport modeling will ultimately lead to an improved basis for predicting TRU migration in the vadose zone to adjacent groundwater supplies.

Research Progress and Implications

As of February, 2000, initial sorption experiments have been performed with Pu(VI) on manganite (MnOOH), a manganese oxide/hydroxide mineral with a structure similar to that of rutile. The mineral was first characterized using a combination of powder X-ray diffraction (XRD) and X-ray absorption fine structure spectroscopy (XAFS) on the Mn K edge. Two other manganese oxide minerals, cryptomelane (KMn_8O_{16}) and hausmannite ($Mn(II)Mn(III)_2O_4$), were also characterized with these techniques for use in upcoming sorption experiments. The sorption studies were carried out in batch mode with manganite that was approximately 30-50 µm in size at an ionic strength of 0.1 M. Experiments were performed at two different pH values (5 and 9.5) under atmospheric conditions. The concentration of Pu(VI) in the sorption experiments was 10^{-4} M.

The amount of plutonium sorbed onto the manganite was determined by liquid scintillation measurements taken before and after the addition of the solid. In all samples over 95% of the plutonium was adsorbed after approximately 10 minutes of contact with the manganite. After 24 hours of constant agitation, approximately 50% of the remaining aqueous plutonium was also sorbed onto the manganite. This sorption process is similar to that of other metal oxides where a very fast initial adsorption step is followed by a much slower adsorption step.

The sorption samples were characterized using XAFS on the plutonium L_{III} edge. The oxidation state of the plutonium after having sorbed onto the manganite was determined by comparing XAFS spectra from the sorption samples to aqueous standard solutions of Pu(IV), Pu(V) and Pu(VI). Approximately 90% of the sorbed plutonium at pH 5 remained as Pu(VI) and the other 10% was reduced to Pu(IV). Likewise, only about 30% of the sorbed plutonium at pH 9.5 remained as Pu(VI) and the rest of the plutonium (70%) was reduced to Pu(IV). There was no evidence of Pu(V) at either pH. Figure 1 shows a representative fit to one of the pH 9.5 samples. The fit is constructed from linear combinations of the Pu(IV), Pu(V) and Pu(VI) standards until the errors of the fit are minimized.

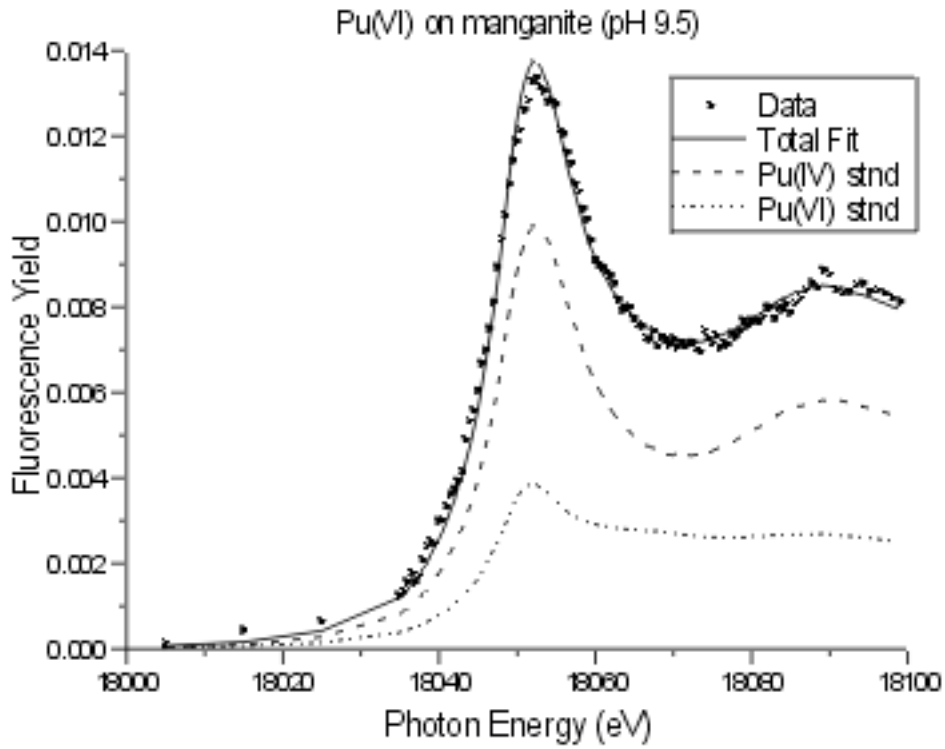


Figure 1. Representative fit to Pu L_{III} XAFS data from the sorption of Pu(VI) on manganite at pH 9.5.

Planned Activities

The manganese minerals will be further characterized to determine their surface area, surface site density and proton exchange capacity. Sorption experiments will be continued to determine the thermodynamic and kinetic parameters governing the sorption of aqueous ions of neptunium and plutonium in well-defined oxidation states on well-characterized mineral surfaces as a function of pH, actinide concentration and ionic strength. These parameters will then be used as input data for reactive transport modeling of TRU in the vadose zone and for the determination of the speciation of neptunium and plutonium in contact with manganese oxide/hydroxide minerals.

References

1) M. C. Duff, D. B. Hunter, I. R. Triay, D. T. Reed, C. R. Cotter, S. A. Aase, P. M. Bertsch, J. Kitten, G. Shea-McCarthy, S. J. Chipera, and D. T. Vaniman, "Oxidation state analyses and mineral associations of sorbed ^{239}Pu on tuff," Preprint (1999).
2) A. Manceau and J. –L. Hazemann, "ALS work 1998-1999," Personal communication (1999).

Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone

Project ID: 70126

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Research Objectives

In this project, basic research integrating macroscopic and spectroscopic studies are being conducted to address the contamination problems associated with radionuclides (Cs^+/Sr^{2+}) at DOE sites (e.g., Hanford, WA; Savannah River Site, Aiken, SC). The focus is on understanding the interfacial reactions responsible for contaminant sorption and associated immobilization and retardation under relevant geochemical (pH ≈ 14; 3 M Na^+ background) conditions. Application of appropriate clean-up technologies requires information on the strength of interaction between the contaminants and solid phases. This study will provide suitable geochemical explanation pertinent to the observed migration characteristics of these contaminants in the vadose zone. The results obtained will find applications in equilibrium and transport models for quantifying radionuclide distribution between solid, colloidal, and dissolved phases. Such models are already in use for predicting future migration of the contaminant plume.

The main objectives of this work are to: i) quantify the rate and extent of radionuclide sorption/desorption on pristine and altered clay surfaces through macroscopic batch and column experiments, ii) investigate dissolution behavior of layer silicates induced by these extreme geochemical conditions using XRD, FTIR, and NMR spectroscopies, and iii) identify the mechanisms of interaction at the molecular level using NMR and XAS spectroscopies.

Research Progress

This report summarizes work after 4.5 months of a 3-year project.

Preparation and Characterization of Clay Minerals

Specimen clay minerals Georgia kaolinite (KGa-2), Wyoming montmorillonite (SWy-2) and Silver Hill illite (IMt-1) were acquired from the Source Clay Minerals Repository at the University of Missouri, and vermiculite from Ward's, NY. The < 2μm size fraction of kaolinite and montmorillonite were collected by dispersion, sedimentation and centrifugation, and the clays were treated to remove surficial metal, oxide and organic impurities prior to repeated homoionic saturation in NaCl solution. Illite and vermiculite were fractionated gravimetrically to obtain a fraction < 115μm, purified and Na-saturated as mentioned above. The clay minerals are stored in aqueous suspension prior to use. The clay minerals have been characterized using solid-state ^{27}Al and ^{29}Si CPMAS NMR spectroscopy.

Sorption Experiments

Preliminary experiments were conducted to determine Cs^+ sorption capacity and $Na^+ \rightarrow Cs^+$ selectivity of the clay minerals as well as ascertain the detection limits of NMR and XAS spectroscopies. Cs-saturation of clay minerals was achieved by equilibrating once with 0.5 M CsCl

[1h], twice with 0.1 M CsCl [1h], and once with 0.05 M CsCl [8d]. Cs-saturated clays were then reacted twice with 0.01 M NaCl to displace Cs^+ from sites with lower $Na^+ \rightarrow Cs^+$ selectivity. A final washing step with 1.0 M NH_4OAc extracted Cs^+ from sites exhibiting highest $Na^+ \rightarrow Cs^+$ selectivity. Table 1 provides the total Cs^+ sorption capacity of the clay minerals and surface excess values after successive NaCl extractions. Highest sorption capacity was observed for montmorillonite followed by vermiculite, illite, and kaolinite. The data in Table 1 indicate that Cs^+ continues to desorb from clay mineral surfaces with increasing NaCl exchange steps. These samples are being analyzed by NMR and XAS spectroscopies to elucidate the local structural environment. To closely simulate the characteristics of REDOX/PUREX waste streams at Hanford, synthetic waste liquor [SWL] with the following composition (Al - 0.1 M; Na^+ - 3 M; NO_3^- - 1.2 M; NO_2^- - 0.9 M; pH^a~14) has been prepared for use in subsequent experiments.

NMR spectroscopy

Solid-state NMR experiments are vital for understanding the local environments of the cations of interest in relation to the framework structure of the clay mineral. Montmorillonite is of interest due to its ability to selectively encapsulate species such as Cs^+ and Sr^{2+}. The structure of montmorillonite is complex and the ^{29}Si MAS spectrum (Fig. 1) results in many overlapping lines. Through the use of double- and triple-resonance solid-state NMR experiments, we are able to focus on specific regions within the montmorillonite structure and identify the type of framework position and cation that is present. Preliminary cross-polarization (CP) experiments involving the transfer of polarization from protons to Si have been performed. Using kaolinite and a hydrated Na-A zeolite as standards, we have been studying the difference in CP from surface hydroxyls compared to water molecules as a function of the contact time used for polarization transfer. The same experiments on montmorillonite with a short contact time (polarization mainly from surface hydroxyls, Fig. 2) and a long contact time (polarization mainly from water molecules, Fig. 3) show differences in the Si spectrum.

Planned Activities

Macroscopic batch experiments involving Cs^+ and Sr^{2+} sorption to specimen clay minerals contacting SWL are being performed as a function of time [1d, 7d, 1-30 months] to determine the rate and extent of radionuclide sorption under Hanford-specific conditions. Dissolution of clay minerals is monitored through measurements of soluble Al/Si and using XRD, FTIR and NMR spectroscopies. These sorption experiments will be extended to uncontaminated sediments obtained from Hanford [Time frame: next 6 months]

TRAPDOR and TEDOR experiments are being developed which will allow for identification of the relationship of Na and Cs cations with the tetrahedral and octahedral Al atoms and the Si atoms of the clay mineral framework. We are pursuing TRAPDOR measurements that will utilize the selective excitations effects of the CP experiments. The excitation is followed by the determination of proximities of the excited species to the Na and Cs cations, to identify whether the cations are near frayed edge sites (Si atoms with hydroxyl groups) or on the basal surface. Planned studies will investigate saturated samples and those subjected to successive extractions [Time frame: next 6-9 months].

X-ray absorption spectra at the Cs L-edge and Sr K-edge for the samples generated from macroscopic experiments will be collected at the bending magnet beam lines X18B at NSLS, Brookhaven National Laboratory. XAS data will help elucidate the coordination environment of the sorbed Cs^+ and Sr^{2+}, the modes of interaction, and the type of sorption complex formed [Time frame: next 6-9 months].

Table 1. Cs^+ sorption capacity and surface excess (q_{Cs}) following repeated extractions with 0.01 M NaCl.

Clay Mineral	Sorption capacity [$mmol_c\ kg^{-1}$]	q_{Cs} [$mmol_c\ kg^{-1}$] 1	2
Kaolinite	36.43±1.87	12.90±3.2	8.55±0.77
Montmorillonite	783.37±0.63	626.73±5.22	538.50±7.23
Illite	150.58±2.87	90.30±2.15	67.96±0.73
Vermiculite	271.00±6.80	190.92±2.04	158.94±1.48

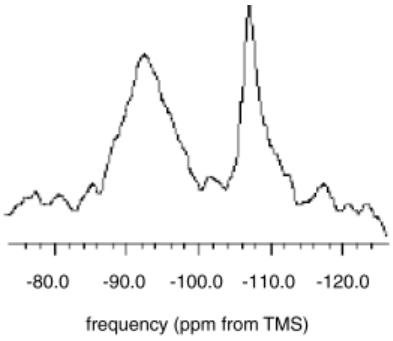

Figure 1. ^{29}Si MAS spectrum of Montmorillonite.

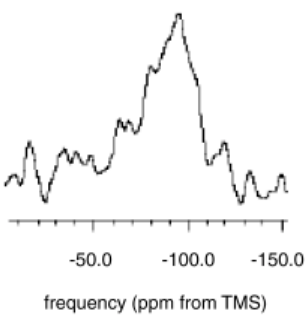

Figure 2. ^{29}Si CP MAS spectrum of Montmorillonite (contact time = 2.5 ms).

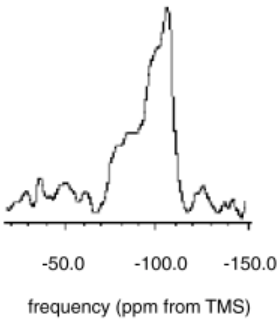

Figure 3. ^{29}Si CP MAS spectrum of Montmorillonite (contact time = 12 ms).

Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone

Project ID: 70050

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Research Objective

The long-term objective of this research is to develop a system for measuring and identifying a wide range of volatile organic hydrocarbons, including organochlorides, at ppb levels *in-situ* in the subsurface ("at-depth") using a fiber-optic REMPI probe in a cone penetrometer. And, to do this in a system that has a fiber-optic Raman probe and an image guide for simultaneous Raman and video imaging of the measurement area. The specific focus of much of the proposed work is to identify and optimize those experimental parameters which effect the *in-situ* determination of organic molecules in the subsurface using resonance-enhanced multi-photon ionization (REMPI). To accomplish this goal we will systematically investigate the dependence of REMPI on laser wavelength, power and other experimental parameters for a variety of high-priority groundwater and vadose zone contaminants to determine optimal measurement conditions. Emphasis will be placed on visible excitation so that the high transmission of fiber-optics at visible wavelengths can be fully utilized. A fiber-optic REMPI system will then be designed and integrated into an existing cone penetrometer system at LLNL. The design will be compatible with existing Raman and fluorescence probes. Fiber-optic probe designs will result from information gained in the first studies, and from previous experience by both the USC and LLNL groups. We will model the performance of different probe designs in a way similar to models we have developed for fiber-optic Raman and fluorescence probes. The specific studies that will be performed are described below. Finally, we will field test the probe in a cone penetrometer. LLNL has considerable experience in this area. This work will also be supported by a cone penetrometer experimentation group at SRL.

In this work we will study the use of both low-order (*e.g.*, 1+1, short wavelength) and high-order (*e.g.*, 2+2 visible-wavelength) REMPI excitation schemes, (described below), for some high priority volatile organic and VOC contamimants to learn the best way to measure these UV-absorbing molecules in the subsurface. This knowledge will be applied to optimization of REMPI for *in-situ* measurements using fiber optics. Also, we will investigate the best optical geometry for the fiber optic launch and collection probes to determine the effect on the signal-to-noise ratio (SNR) and how best to integrate REMPI into existing fiber-optic probes that are used for Raman and fluorescence measurements. Finally, we will study the REMPI 1+1 and 2+2 signals for different sample matrices as a function of excitation wavelength across a broad spectrum. A result of this study should be a determination of the optimal excitation and collection conditions and sampling methods for organic contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for REMPI sampling.

Background

The long-term goal of this project is to develop a system to measure VOCs in the subsurface, *in-situ*, at both very low concentrations (vapor phase) and at high concentrations (liquid phase, NAPLs) using a fiber-optic probe. Visible wavelength REMPI will be developed for low level concentrations, whereas Raman scattering is already available for liquid phase measurements. REMPI has sensitivity

comparable to fluorescence but can be used to measure non-fluorescent compounds. However, it is more selective than fluorescence and has been used to measure trace levels of molecules in complex matrices such as flames and plasmas.

Volatile organic chemicals are found in almost every natural water source on earth. This is primarily due to the poor disposal practices of the past and accidental spills. For example, in 1988 it was estimated that 33.1 million pounds of benzene and 344.6 million pounds of toluene were released into the environment.[14] Once these chemicals have been introduced into the ground, they begin to partition into the water supplies and collect in wells and other storage areas. Since clean-up of contaminated water supplies is very expensive, it is desirable to develop techniques that can be used on-site to rapidly identify the organic pollutant as well as the amount of contaminant present.

Gas chromatographs (GC) are the most commonly used instruments for the detection of trace volatile organic compounds in water samples.[15,16] For these analyses, there is typically a preconcentration step that extracts the sample from the water and requires a great deal of time and effort. This extraction can be through various methods such as activated charcoal, liquid/liquid extraction, or solid phase microextraction (SPME).[17,18] Since both the preconcentration and GC separation steps require time and sample preparation, it would be favorable to have a fast, remote analysis capability.

REMPI Background

Resonance enhanced multiphoton ionization (REMPI) is a useful technique for obtaining both qualitative and quantitative information about volatile organic pollutants. In addition to the applications mentioned above this technique has been used extensively as a selective ionization source for mass spectrometers[6-12b] as well as in spectroscopic combustion analysis[13-16b] in the last couple of decades. In the REMPI technique, a tunable pulsed laser is used to electronically excite a specific molecule using one or more photons. A 1+1 excitation scheme refers to a two-photon process where one photon creates the excited molecule and another photon ionizes the molecule from the excited state. In a 2+2 excitation scheme two photons are used to excite then ioinize the molecule — a four-photon process. As shown in Fig. 1 the main difference between resonance ionization and laser ionization (LI) is that an electronic excited state is involved in REMPI. This not only results in very large enhancements but is also the reason REMPI can be used as a qualitative technique. While excited, the subsequent absorption of an additional photon(s) then ionizes the molecule. Ionization probability is much larger for REMPI than for LI because the "real" state in REMPI is much longer lived than the "virtual" state in LI. Also, because of the large enanecements in REMPI, even four-photon excitation schemes provide very high sensitivity. And, it is important to point out that REMPI requires low to moderate laser power.

Once ionized, an electrode that is biased at a high positive or negative potential is used for efficient electron or ion collection. The current created by these electrons/ions flowing to the electrode is then measured as a voltage drop across a "leak resistor," and the resulting voltage is therefore proportional to the concentration of the specific species being ionized. Due to the non-linear nature of this technique it is important to have high power densities, small focused beam, near the collection electrode. A higher power density increases the probability of ionizing the specific molecule of interest. Although the electrode is typically biased at 800-1000 V, the current is extremely low requiring only a very small relatively well-regulated power supply.

In the REMPI technique a relatively low power pulsed laser is focused to a small spot to induce molecular ionization in a multiphoton, **N**-photon, process where the multiphoton energy exceeds the ionization potential. In nonresonant multi-photon ionization (MPI), the ionization cross section, d_N, is low but increases with increasing photon flux, I, with d_N being proportional to I^N. By tuning the laser so that the energy sum of the **N** photons is in resonance with a *real* intermediate resonance state, E_f, (REMPI) the ionization cross section is enhanced by up to 10^6 if the $E_o \rightarrow E_f$ transition is an allowed transition of the molecule (E_o is the ground state, E_f is the energy of the resonant electronic state). This is shown schematically in Fig. 1. The greatly enhanced ionization cross section in REMPI results in extremely high ion yields and thus very high sensitivity. Because ions can be collected very efficiently this technique is one of the most sensitive *in-situ* methods for applications such as combustion diagnostics.[23-25]

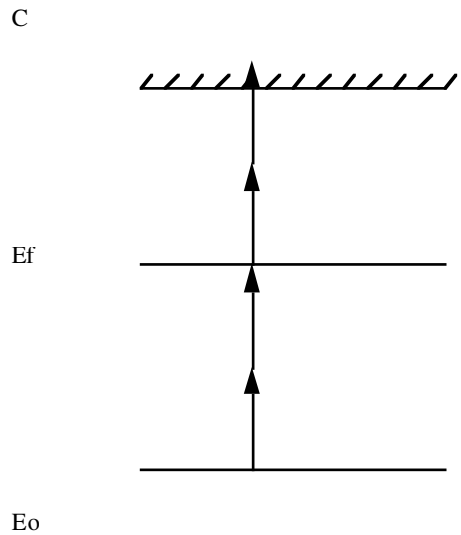

Fig. 1. Energy level diagram showing the resonant ionization of a molecule through a multi-photon ionization process.

REMPI is widely used to obtain multiphoton spectra because of its high sensitivity and simplicity. Although there have been a few reports of its analytical use most reports have focused on studying the resonance enhanced multiphoton ionization process itself rather than its use for quantifying chemical species. However, applications of this technique are beginning to appear. For example the spectral sensitivity and selectivity of resonance-enhanced multi-photon ionization spectroscopy for detecting various chloroethylenes has been demonstrated and REMPI has been used to measure many radical species including O, H, OH, CH, CO, HCO, CH_3 and chlorinated flame radicals.[23-31] REMPI has been used most widely for measuring gas-phase spectra of simple molecules, molecule fragments and radical species. However, as indicated above recent studies have used REMPI for organic molecules, and we recently demonstrated its use for measuring volatile organic molecules *in-situ*.

Due to its sensitivity and qualitative capabilities, REMPI, is an excellent technique for remote analysis of many types of volatile organics in the environment. In previous related work, we showed that by using optical fibers it is possible to introduce high power laser pulses to a remote area.[17c] A REMPI probe is made by simply placing a small biased electrode near the focus of this laser pulse, making it possible to make a simple and remote probe that can be placed down a well or other inaccessible area for remote trace analysis. Most organic contaminants absorb most strongly in the UV. For example, BTEX compounds (*e.g.*, benzene, toluene, ethylbenzene and xylenes) absorb strongly in the 240 to 280 nm range. In previous work we used 266 nm excitation in a 1+1 excitation scheme to measure toluene at ~1 ppb with a fiber-optic probe. However, in that work we also showed that four-photon REMPI, in a 2+2 excitation scheme at 532 nm, could be used to measure toluene at concentrations around 10 ppb. This result was achieved using a relatively small laser with ~25 mJ of power per pulse. This is an important result because it demonstrates that REMPI can be used to measure low levels of organic contaminants with a small visible-wavelength laser, and at wavelengths that are compatable with fiber-optic probes. The use of visible wavelengths also makes REMPI compatable with existing fiber-optic Raman and fluorescence probes, and thus compatable with cone penetrometry.

Before REMPI can be applied to the measurement of subsurface contaminants it is necessary to make fundamental measurements to characterize it for this purpose, especially comparing 1+1 and 2+2 excitation schemes. And, the optimal laser power for the analytes of interest. The optimal wavelength for a REMPI measurement does not always correspond to the maximum sample absorbance, because of lower background ionization in regions of lower absorbance,[33] or rapid relaxation

to spin-forbidden states[2]. Although these results were obtained at low pressure and the experiments aren't too related, it is not known if similar results, especially background ionization, might be observed in one-atmosphere experiments. As mentioned above, most applications of REMPI have been for molecular fragmentation in mass spectrometry. In this application systematic studies of laser wavelength have rarely been done. Most detailed excitation wavelength studies have been carried out for flame species.[19-22] Thus, an important part of this work is to study the excitation wavelength dependence of the REMPI signal for the contaminants of interest. We also need to determine what other experimental parameters can be optimized for an analytical measurement, and to evaluate potential interferences. The excitation wavelength dependence of REMPI signals will be determined for several high-priority pollutants using both 1+1 and 2+2 excitation schemes. REMPI signals as a function of sample matrix, sample state (dry, wet, etc.), and excitation wavelength have not been obtained in a systematic way for the compounds of interest and such studies are crucial to making this a reproducible analytical technique. No fiber-optic REMPI studies have appeared in the peer-reviewed literature. So, it is difficult to predict the limitations that might be caused by the use of fiber-optic probes.

We will investigate the use of fiber optics to deliver the laser to the sample and to collect the resulting ion emission using a small, ~1-mm diameter, bead electrode connected to the surface instrument by a small insulated wire. Recent results in our laboratory demonstrate that sufficient laser power can be delivered to the sample by a fiber optic to make very sensitive REMPI measurements without damaging the optical fiber. The technique has the potential for identifying subsurface organic contaminants at very low levels and rapidly. In combination with a fiber-optic Raman probe this allows organic contaminants to be measured and identified over a wide concentration range. The use of fiber optics for both REMPI and Raman spectroscopy could minimize the need for grab-sampling. In this work we will study the REMPI excitation wavelength dependence at UV and visible wavelengths for different matrices to better understand how to optimize the signal. Also, we will investigate fiber-optic probe geometries to determine the effects of the fiber on the SNR and optimal wavelength and power. Finally, we will investigate the incorporation of both REMPI and Raman into a cone penetrometer-compatable probe, that is also outfitted with an image guide for direct visualization of the sampling region. A result of this study should be a determination of the optimal excitation wavelengths and sampling conditions for organic contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for REMPI sampling.

Our preliminary REMPI work is quite exciting.[12,13] The toluene detection limit measured *in-situ* with a fiber-optic REMPI probe is ~1ppb using a 1+1 excitation scheme at 266 nm, well below the regulatory limit. And, using a 2+2 excitation scheme at 532nm, the detection limit was ~10 ppb. A 90-s analysis was shown to be sufficient to identify and quantify toluene, even in a complicated sample like gasoline, and with little or no interference from benzene. The laboratory-built fiber-optic REMPI probe is a small hand-held device that is readily adaptable for field work.

REMPI Results

In recent work a simple fiber-optic probe suitable for remote measurements of ppb levels of aromatic hydrocarbons using resonance enhanced multi-photon ionization (REMPI) was developed.[12,13] Optical fibers transport the laser pulse to the sample and a small wire transfers the ion current to a digital oscilloscope. The measurement takes about one minute to perform, requires no sample preparation, and can be made through optical windows. The limit of detection for toluene was ~1.4ppb using 1+1, 266 nm excitation, and ~10 ppb using 2+2, 532 nm excitation. We are currently extending this to the measurement of compounds, such as VOCs, that absorb at even shorter wavelengths.

Fiber-Optic REMPI Probe. In preliminary work a simple fiber-optic probe suitable for remote analysis using resonance enhanced multiphoton ionization was developed and used to determine the toluene concentration in aqueous gasoline samples via a head space measurement. An optical fiber transmits a high power laser pulse (266 nm) to the sample, ionizing it, and the subsequent ions are collected with a platinum electrode. Measurements take approximately 1.5 minutes to perform, require no sample preparation, and have been demonstrated over distances of five meters. The limit

of detection for toluene in water using this probe is 1.54 ± 0.02 ppb (wt/wt). In addition to the 1+1 excitation, the feasibility of a 2+2 excitation scheme using 532 nm has been investigated.

Sample preparation: For this study, aqueous toluene and gasoline samples were prepared by placing equal volumes of toluene or gasoline (Shell 93 octane) and deionized water in a sealed container and stirring them vigorously for several days. The water portion of the sample was then extracted and placed in a sealed container. This solution was saturated with toluene, giving a concentration of 550 ppb toluene.[18h] To cover the concentration range of toluene that was measured in this paper, 0 ppb to 550 ppb, dilutions of this saturated solution were made using deionized water. For measurements using the fiber-optic REMPI probe, spiked water samples were placed in a petri dish and covered with a plastic air tight lid with a small hole in the center. The probe was placed over this hole and sealed and the headspace above the sample, and allowed to equilibrate for 20 minutes with the probe in place. For experimental optimization experiments of electrode bias voltage and laser power, neat toluene or toluene diluted in methanol was injected into the sealed cell and allowed to evaporate completely. For measurements of dry vapor in a sealed cell the concentration of toluene is reported in ppb (mol/mol) with respect to air. For measurements of aqueous solutions of toluene concentrations are reported as ppb (wt/wt).

All of the data are shown without averaging or smoothing. For all measurements, the intensity of the REMPI signal is based on peak height after a fixed delay time from the laser pulse, and all error bars displayed represent one standard deviation of five replicate measurements. A linear best fit of the data was calculated, and the detection limit is taken as 3 times the standard deviation of the blank divided by the slope (*e.g.*, a "3σ" detection limit).

Fiber launch conditions: One difficulty in using fiber optics for REMPI measurements is avoiding damage to the excitation fiber. Focusing the laser on the tip of the fiber can chip the face, or in some cases completely destroy the fiber's tip. In addition, it was also found that if too much power was launched into the fiber or into the cladding of the fiber, catastrophic damage to the core/cladding interface was observed. Since REMPI is a non-linear process it is important to launch as much power down the fiber as possible. By using a pinhole at the fiber tip, and placing the fiber just beyond the focus of the laser, it was found that optical fibers can withstand approximately 200 mJ/pulse at 532, and this launch worked very well for REMPI experiments.[32,37]

REMPI signal intensities for a particular sample depend on several different parameters such as electrode voltage, excitation fiber, laser power and excitation wavelength. As these parameters are sample dependent, there is no optimized setting for all measurements, but we have investigated these parameters for toluene and gasoline measurements. The first of these parameters, electrode voltage, is very important for signal collection, and is primarily dependent on the probe design. One of the main reasons for the great sensitivity of REMPI is the collection efficiency of the signal. Because the signal being collected is charged particles, it is possible to achieve a collection efficiency of approximately 100%.[13b (above)] Thus, it is important to optimize the bias voltage of the electrode to maximize signal while reducing error from small voltage fluctuations. This optimization was performed by injecting the equivalent of 1.78 ppth of toluene into the sealed cell, allowing it to evaporate, and then monitoring the ion signal as we varied the probe voltage from 500 to 1200 volts. Three distinct regions were evident from this data. At voltages lower than 800 V, there is a dramatic increase in signal due to enhanced collection efficiency and reduced electron/ion recombination. Between 800 and 1100 V, a plateau region exists where the maximum collection efficiency occurs. Above 1100 V, the ion signal once again increases dramatically with increasing probe voltage, because of the cascade effect. Based on the results of this experiment +1000 V was used for all remaining measurements.

Power density is crucial to obtaining quality REMPI signals and thus high sensitivity. It is important both to transmit the maximum amount of excitation light through the fiber, as well as to have a small spot size near the electrode tip. Optimizing the power density of the spot near the electrode is dependent on the diameter and type of excitation fiber used. Therefore we investigated using a low •OH content 1000 mm fiber, a high •OH content 910 mm fiber and a high •OH 550 mm fiber (Fig. 2). The low •OH content fiber, with a 1000 mm diameter, has its greatest transmission efficiency in the region of 350 nm to 800 nm. However, this fiber costs less than a fiber of comparable diameter that has a transmission maximum in the ultraviolet region. When using this fiber, 6.1 mJ of 266 nm

light were launched into the fiber and approximately 4.0 mJ were measured at the distal end. By injecting various amounts of toluene into the cell and monitoring the ion signal while using this fiber for excitation it was possible to obtain a calibration curve for toluene in the vapor phase. From this calibration, the sensitivity was found to be 0.045 ± 0.004 mV/ppb of toluene corresponding to a detection limit of 4.4 ± 0.4 ppb (mol/mol) of toluene in air. Next, we performed the same experiment using a high ∑OH content, 910 mm fiber with better UV transmission. For this experiment, 6.1 mJ of 266 nm light was launched into the fiber and 5.4 mJ was measured at the distal end. The sensitivity of the probe increased to 0.0636 ± 0.0006 mV/ppb of toluene with a limit of detection of 1.005 ± 0.009 ppb (mol/mol). Next experiments were done to determine the optimum fiber diameter. We found that a 550 mm fiber with a high •OH content could transmit the same amount of power as the larger fibers. Using this fiber allowed for a tighter focus near the electrode and therefore a greater power density. As a result, an increase in sensitivity to 0.0912 ± 0.0008 mV/ppb and a lower detection limit of 0.858 ± 0.0007 ppb (mol/mol) were obtained using the 550 mm fiber.

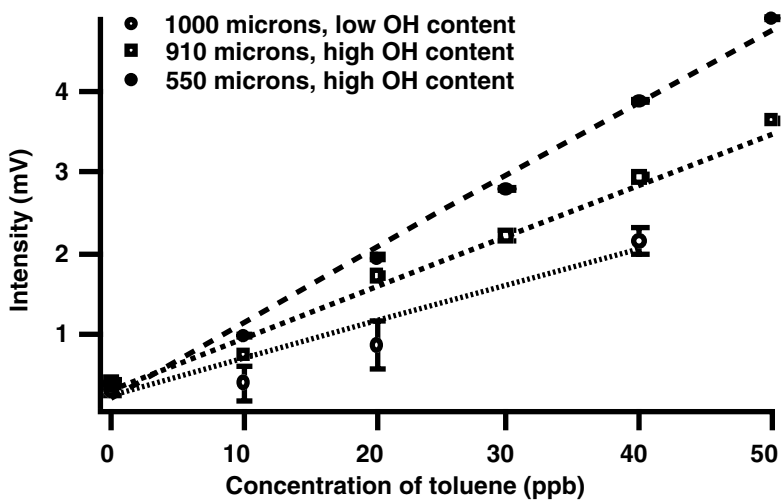

Fig. 2. The effect of optical fiber type and diameter on sensitivity of REMPI signal. Circles denote the 1000 μm low •OH content fiber, squares denote the 910 μm high •OH content fiber and triangles denote the 550 μm high •OH content fiber. Excitation of the sample was accomplished by launching 6.0 mJ/pulse of 266 nm light into the specific fiber. Each point represents the average of five measurements with error bars showing ± one sample standard deviation.

To determine the dynamic range different amounts of toluene were injected into the cell covering a concentration range from 1 ppb to 10 ppm (mol/mol). After the toluene evaporated, five measurements were made at each concentration. These results are shown in Fig. 3. From this plot it is evident that the REMPI signal remains linear over approximately 3.5 orders of magnitude of toluene in air. Therefore this is an excellent technique for remotely monitoring toluene concentrations over the ppb to a few ppm levels using fiber optics.

Calibrations experiments were also carried out for aqueous-phase toluene using the fiber-optic REMPI probe. Fig. 4 shows the calibration of toluene in spiked water samples using a 1+1 excitation scheme at 266 nm (open circles). For these measurements, the spiked water samples were placed in a petri dish so that the amount of liquid was equal in volume to the headspace volume above the sample. After approximately 10 minutes, equilibrium between the liquid toluene and the vapor toluene was reached and a measurement was taken. This was repeated for samples ranging in concentration from 5.5 ppb to 275 ppb (wt/wt) toluene. For this calibration we obtain a sensitivity of 0.137 ± 0.002 mV/ppb. This is significantly better than that obtained using the cell described earlier.

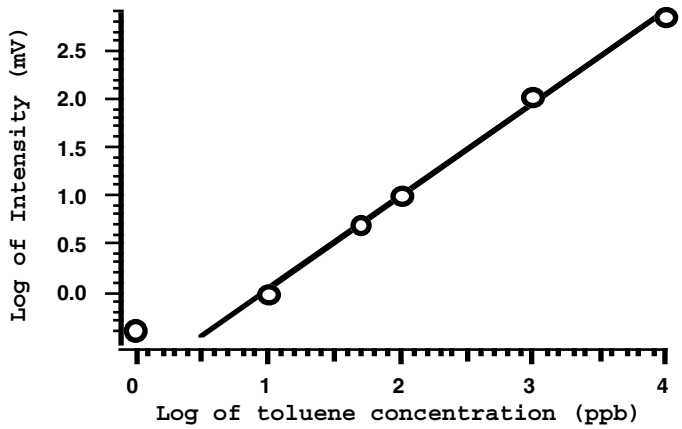

Fig. 3. Dynamic range of REMPI technique for measurement of toluene. A 550 mm high •OH content fiber was used for these measurements with the collection electrode biased at +1000 V and 266 nm excitation. Each point in this curve represents the average of five measurements with error bars showing ± one sample standard deviation.

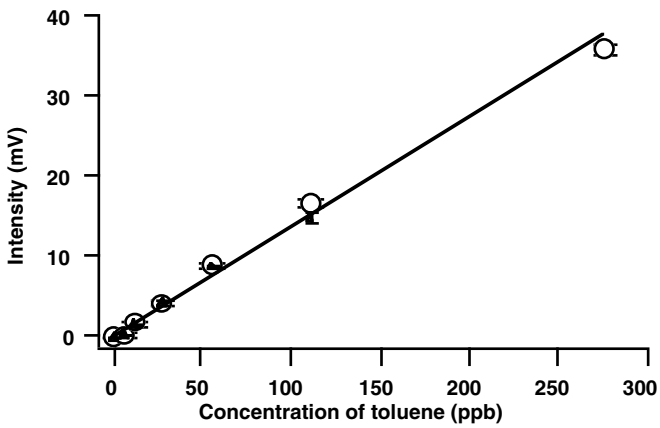

Fig. 4. Calibration of toluene spiked water samples (open circles), and the toluene from gasoline spikedwater samples (dark triangles). For both calibrations a 550 mm high •OH content fiber was usedfor these measurements with the collection electrode biased at +1000 V and 266 nm excitation.Each point in this curve represents the average of five measurements with error bars showing± one sample standard deviation.

While all the reasons for this enhancement have not been totally investigated, the primary reason for this difference is that the electrode in the probe has an additional insulating layer not present in the cell. This additional insulation prevents short circuiting of the probe and therefore both increases the ionization signal and decreases the background. From this increase in signal to background, we lower our detection limit of toluene to 1.54 ± 0.02 ppb of toluene in water.

Since gasoline is often found in ground water samples, and a major constituent of gasoline is toluene, we also tested our probe using water samples spiked with gasoline. These gasoline spiked samples were prepared by the same procedure used for the toluene, and therefore should have very similar concentrations of toluene in the saturated sample. This calibration is shown in Fig. 4 (dark triangles) and the concentration listed on the abscissa is the concentration of toluene in the water, based on a saturated concentration of 550 ppb. It is obvious from this calibration that the sensitivity and detection limit of toluene from the gasoline spiked samples is similar to toluene spiked water samples (0.132 ± 0.004 mV/ppb and 1.88 ± 0.06 ppb). This shows that there are no significant

interferences from the other constituents in gasoline. To verify this, we tested benzene, hexane, heptane, and methanol using our probe with 266 nm excitation and found no appreciable signal from neat solutions of these compounds. The lack of interference from these samples is explained by the fact that the resolution of the various vibronic bands that occurs in the vapor phase is sufficient to prevent significant ionization of these compounds. In addition to this, and maybe more importantly, the solubility of toluene in water is much greater than all other major constituents of gasoline except methyl tertbutyl ether, and benzene.[36]

2+2 Excitation, Preliminary Results. Even the best high •OH content optical fibers transmit more efficiently in the visible than in the ultraviolet. Because of this, we investigated the use of higher order excitation schemes using our probe. To do this 532 nm light was launched into the 550 mm fiber and approximately 20 mJ/pulse were measured at the distal end. This light was then excited and ionized the toluene from the spiked water samples via a 2+2 excitation scheme. The results are shown in Fig. 5 and demonstrate the feasibility of using this higher order excitation for much more distant measurements than five meters. While the sensitivity, 0.0139 ± 0.0005 mV/ppb, and detection limit, 8.6 ± 0.3 ppb (wt/wt), for this experiment are nearly an order of magnitude lower than for the 1+1 excitation scheme, these results are very promising. It is possible to launch much greater laser powers at 532 nm through fibers larger than 550 mm and could possibly allow for comparable sensitivity as well as increased measurement distances.

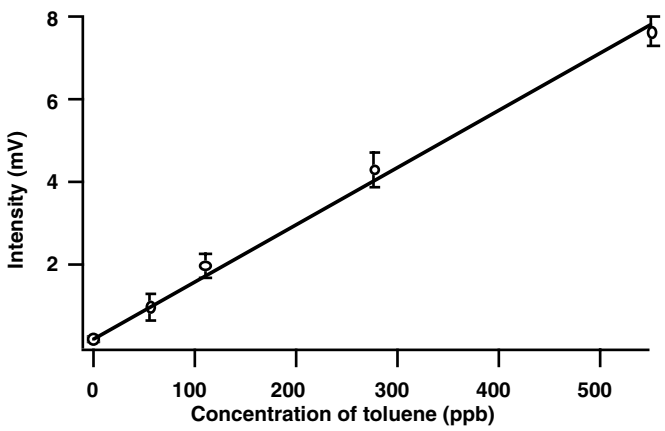

Fig. 5. Calibration of toluene spiked water samples with a 550 mm high •OH content fiber was used for these measurements with the collection electrode biased at +1000 V and 532 nm excitation. Each point in this curve represents the average of five measurements with error bars showing ± one sample standard deviation.

Pulsed Fiber-Optic Excitation. One difficulty in using fiber optics to measure LIBS spectra is avoiding damage to the excitation fiber. Focusing the laser to a tight spot on the fiber tip can chip the surface or in some cases completely destroy the fiber. Catastrophic damage at the core cladding interface was observed if the power were too high, if the fiber were misaligned, or if laser spots were too small. For the paint sample measurements, power levels of 4.2 mJ and 19.0 mJ were typically measured at the probe tip, the end nearest the sample, for the 600 mm and 1000 mm excitation fibers, respectively. In the case of a 600 mm excitation fiber, power levels as low as 1 mJ were observed to produce a plasma at the sample. To minimize fiber damage the laser was used at the lowest power possible and was loosely focused using an f/8 lens so that the spot was relatively large compared to the fiber tip. The decreased power density, together with the use of a small pinhole in front of the fiber tip, eliminated fiber damage for input powers as high as 200 mJ. This arrangement resulted in 40 to 50% throughput to the fiber-optic probe tip, depending on the size of the excitation fiber.

Recently we described the use of a LIBS probe for determining Pb in paint *in-situ*.[37] The probe used for this work was a modified fiber-optic Raman probe. Although it was not optimized for LIBS

measurements we were able to measure 0.014% Pb in latex paint, on a dry-weight basis, with relative sample standard deviations of 5 to 10%. The measurement takes less than one minute to perform, requires no sample preparation, and can be made through overlayers of non lead-containing paint. The use of a fiber-optic probe with separate excitation and collection fibers minimizes sample alignment and allows coupling of the probe to a conventional spectrometer using simple optics. The proposed research should provide the basis for designing much better LIBS probes.

REMPI System. The REMPI system (Fig. 6) consists of a Q-switched Nd:YAG laser operating at either the second or fourth harmonic (Continuum Model Surelite III operating at 532 nm, or New Wave Research Model MiniLase-20 operating at 266 nm), a high voltage power supply (Gamma High Voltage Model RC5-30P), the probe/collection electronics and a fast digital oscilloscope (LeCroy Model 9350L). The high power laser pulse is first launched into the optical fiber. This launch was described in detail in previous works.[17c] Laser light is transmitted through the fiber to the probe where it is focused to a point, ionizing the analyte. Electrons created from this ionization are then collected on a platinum electrode biased at +1000 V. The current created by the collection of these electrons is then run through a 250 kW resistor and the resulting voltage drop across the resistor is measured using a 1MW coupled 500 MHz digital oscilloscope. Data shown is the average signal from 1000 laser shots at 10 Hz for a total acquisition time of approximately 1.5 minutes. The laser power at the probe tip was typically 5.4 mJ/pulse (266 nm) or approximately 20 mJ/pulse (532 nm), depending on the excitation wavelength used.

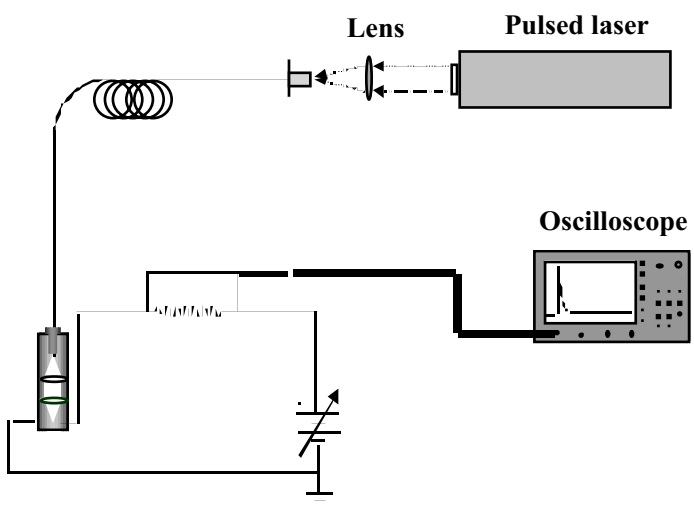

Fig. 6. Schematic diagram of REMPI apparatus showing fiber-optic launch and collection electrode

Fiber-Optic Probe

A unique aspect of our REMPI system is the use of a fiber-optic probe that delivers the laser beam to the sample, allowing remote measurements to be performed easily. The probes we have used thus far are simple modifications of existing designs that have been used in our group for Raman and LIBS spectroscopy.[35,37] The use of an optical fiber for laser excitation and a platinum electrode for signal collection gives the probe setup its simple and remote capabilities. In preliminary work, three different excitation fibers were tested, with core diameters of 1000 mm, 910 mm and 550 mm. Fibers were typically 5 m in length for UV measurements, and the effect of different •OH contents was also examined. Laser light was focused into the excitation fiber using a f/4 lens. Care is taken to eliminate damage to the input face of the fiber by placing a pinhole at the fiber tip that is just slightly smaller than the fiber core diameter (500 mm diameter in the case of a 550 mm fiber).

A cross section of the probe is shown in Fig. 7. The excitation fiber is located in the top of the probe housing, which is made out of aluminum, and the transmitted light is collimated using an f/1.5 fused silica lens. This collimated light is focused to a small spot within 1 mm of the electrode tip using another f/1.5 fused silica lens. Electrons created from the ionization of the sample are collected by the electrode that is biased at +1000 V with respect to the aluminum housing of the probe. The current created by the flow of electrons to the electrode is measured as a voltage drop across a "leak" resistor using a digital oscilloscope.

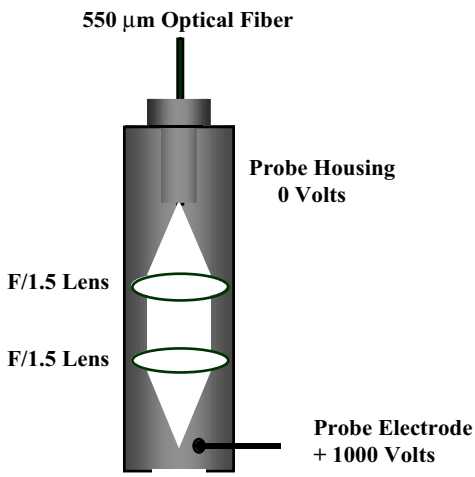

Fig. 7. Detail of the fiber-optic REMPI probe. The lens are 1-inch diameter f/1.5 plano convex, and the platinum electrode is biased at +1000 V with respect to the aluminum housing.

Penetrometer Compatible, Fiber-Optic REMPI Probe Design: LLNL

Background: LLNL has had considerable experience designing and fielding penetrometer deployable sensing technologies, including a chemical TCE sensor and Raman probe. These systems, although both capable of *in-situ* sampling from a cone penetrometer assembly, were significantly different in their base configuration. The TCE sensor operated on colorimetric principles. In the basic sensor design, optical fibers are used to remotely monitor a quantitative, irreversible chemical reaction that, upon exposure to TCE, forms products that absorb certain wavelengths of light. The sensor system has three major components: a miniature pumping and delivery system, an electro-optic readout device for monitoring the transmission of the sensor, and the sensor itself. The system design allows consecutive measurements to be taken at short intervals in and on-demand basis; control and monitoring are done remotely. The small reaction volume of the sensor allows a large number of measurements to be made before the reagent reservoir must be recharged. The reagent delivery system was designed to fit into a standard penetrometry cone (Fig. 11, next page). Two syringe plungers are fixed with respect to one another and simultaneously driven by a motor and a screw, allowing spent reagent to be captured in the empty syringe as fresh reagent is delivered to the sensor. The reagent delivery system and sensor housed in the penetrometer cone are isolated from the environment until a measurement depth is reached. The TCE sensor is then exposed to soil vapors by means of a removable and disposable ground-penetrating tip. The cone is driven to the desired depth and then retracted by 15 cm, leaving the removable tip behind. This creates a void, and exposes the sensor to soil vapors. An optical/electrical cable provides communication from the ground surface to the sensor. This system was successfully tested in multiple field tests at Savannah River Site, yeilding *in-situ* measurement of TCE in the parts-per-billion range (ppb). LLNL also designed and constructed a hardened fiber optic Raman probe and housing to provide *in-situ* characterization of underground storage tanks at the US Department of Energy Hanford site. The Cone Penetrometer

Fiber Optic Spectroscopy Probe Assembly consists of three major components: a penetrometer compatible probe housing, an optical Raman probe, and a window assembly The probe housing is designed to be an integral unit of the CP, supporting the load of a 40 ton vertical push. The probe housing provides a means of optically aligning and locking a fiber optic spectroscopy probe along its vertical axis and a housing for the window assembly along its radial axis. The probe housing also contains cable-way passages, providing a means for electrical cabling to additional sensors, such as the envisioned REMPI electrodes, in the penetrometer tip as needed. Optical communication between the vertically seated Raman probe and the environment is accomplished by the window assembly. The window assembly houses a sapphire window that provides optical access to hazardous sample material without compromising mechanical strength or chemical resistance. A focusing/collimating lens that is housed within the window assembly provides control over the field of view and the depth of penetration of the laser beam in the sample. A single fiber optic cable provides laser input to the probe. A seven fiber optic bundle collects the signal. Seven collection fibers are used rather than one both to increase the collection area and therefore efficiency of the probe and to allow for use of a larger laser spot size (4 mm) when interrogating the sample. A larger spot size results minimizes the efffect of inhomogeneous grain size, resulting in increased signal to noise. The collection fibers are filtered with a long pass filter to remove scattered laser light; the laser excitation fiber is filtered with a laser band pass filter to remove silica Raman generated in the optical fiber. The Raman cone penetrometer probe was successfully tested in a vessel containing tank waste simulant at Hanford.

References Cited

1 S.M. Angel, K. Langry, J. Roe, B.W. Colston Jr., P.F. Daley, and F.P. Milanovich, "Preliminary Field Demonstration of a Fiber-optic TCE Sensor," in *Proceedings of SPIE '90*, *Chemical, Biochemical, and Environmental Fiber Sensors II*, San Jose, CA, Vol. 1368, p. 98 (1990).

2 Marshall A., Ledingham, K.W.D., and Singhal, R.P., *Analyst*, 1995, **120,** 2069.

3 Peng, W.X., Ledingham, K.W.D., Marshall, A., and Singhal, R.P., Analyst, 1995, 120, 2537.

4 Weickardt, C., Boesl, U., and Schlag, E.W., Anal. Chem., 1994, 66, 1062.

5 Pratt, S.T., Poliakoff, E.D., Dehmer, P.M., and Dehmer, J.L., J. Chem. Phys., 1983, 77, 65.

6 Loge, G.W., Tiee, J.J., and Wampler, F.B., J. Chem. Phys., 1983, 79, 196.

7 Tjossem, P.J.H., and Smyth, K.C., J. Chem. Phys., 1989, 91, 2041.

8 Rottke, H., and Zacharius, H., Opt. Commun. 1985, 55, 87.

9 Marshall, A., Clark., Jennings, R., Ledingham, K.W.D., and Singhal, R.P., Meas. Sci. Technol., 1991, 2, 1078.

10 Peng, W.X., Ledingham, K.W.D., Singhal R.P., and McCanny, T., Analyst, 1998, 123, 1035.

11 Marshall, A., Clark., A., Deas, R.M., Kosmidis, C., Ledingham, K.W.D., Peng, W., and Singhal, R.P., Analyst, 119, 1719.

12 Brian M. Cullum, and S. Michael Angel, "Fiber-Optic Resonance Enhanced Multiphoton Ionization (REMPI) Probe for the *In-situ* Detection of Volatile Organic Pollutants," accepted for publication in *Appl. Spectrosc*., 1999.

13 Brian M. Cullum and S. Michael Angel, "Development of a fiber optic REMPI probe for environmental contaminants," *SPIE Proceedings*, Vol. **3534-06**, November 1-5, Boston, MA (1998).

14 McGrath, E. M.; Booksh, K. S.; Breen, J. J. In *Process Analytical Chemistry*; McLennon, F.; Kowalski, B. R., Eds.; Chapman-Hall: New York, **1995**.

15 Neff, J. M. *Chem. Eng. Prog.* **1987**, 83, 27-33.

16 Dean, J. R.; Tomlinson, W. R.; Makovskaya, V.; Cummings, R.; Hethridge, M.; Comber, M. *Anal. Chem.* **1996**, 68, 130-133.

17 Potter, D. W.; Pawliszyn, J. *J. Environ. Sci. Technol.* **1994**, 28, 298.

18 Zhang, Z.; Pawliszyn, J. *J. High Resolut. Chromatogr.* **1993**, 16, 689.

19 Cool, T. A. *Appl. Opt.* **1984**, 23, 1559-1572.

20 Tjossem, P. J. H.; Cool, T. A. *Chem. Phys. Lett.* **1983**, 100, 479-483.

21 Mallard, W. G.; Miller, J. H.; Smyth, K. C. *J. Chem. Phys.* **1982**, 76, 3483-3492.

22 Meier, U.; Kohse-Höinghaus, K. *Chem. Phys. Lett.* **1987**, 142, 498-502.

23 Bernstein, J.S., Fein, A., Choi, J.B., and Cool, T.A., and Sausa, R.C., Howard, S.L., Locke, R.J., and Miziolek, A.W., *Combustion and Flame* **1993**, *92*, 85.

24 Smyth, K.C., and Taylor, P.H., *Chem. Phys. Lett*. **1985**, *122*, 518.

25 Meier, U., and Kohse-Hoinghaus, K., *Chem. Phys. Lett*. **1987**, *142*, 498.

26 Goldsmith, J.E.M., *Opt. Lett* **1982**, *7*, 437.

27 Tjossem, P.J.H. and Cool, T.A., *Chem. Phys. Lett*. **1983**, *100*, 479.

28 Goldsmith, J.E.M., *J. Chem. Phys.* **1983**, *78*, 1610.

29 Mallard, W.G., Miller, J.H., and Smyth, K.C., *J. Chem. Phys.* **1982**, *76*, 3483.

30 Rockney, B.H., Cool, T.A., and Grant, E.R., *Chem. Phys. Lett.* **1982**, *87*, 141.
31 Smyth, K.C., and Mallard, W.G., *J. Chem. Phys.* **1982**, *77*, 1779.
32 Marquardt, B. J.; Cullum, B. M.; Shaw, T. J.; Angel, S. M. *SPIE Proceedings* **1997**, 40. 3105, 203-212.
33 Rhodes, G., Opsal, R.B., Meek, J.T., and Reilly, J.P., Anal. Chem., 1983. **55**, 280.
34 Burns, S. E., and P. W. Mayne, *Penetrometers for Soil Permeability and Chemical Detection*, Report GIT-CEEGEO-98-1, Georgia Institute of Technology, 143 p., 1998.
35 M.L. Myrick and S.M. Angel, *Appl. Spectrosc.*, **1990**, *44*, 565-570.
36 American Petroleum Institute. "Literature Survey: Hydrocarbon Solubilities and Attenuation Mechanisms," Publication # 4414, **1985**.
37 Marquardt, B. J.; Goode, S. R.; Angel, S. M. *Anal. Chem.* **1996**, 68, 997-981.
38 S.M. Angel, and M.L. Myrick, in *Proceedings of SPIE OE/Fibers '89 Symposium*, paper **1172**-04, Boston, MA, September, 1989.
39 M.L. Myrick, S.M. Angel, and R.A. Desiderio, *Appl. Optics*, **29**, 1333 (1990).
40 S.M. Angel, and M.L. Myrick, *Appl. Opt.* **29**, 1350 (1990).
41 M.L. Myrick and S.M. Angel, *Appl. Spectrosc*. **44**, 565 (1990).
42 Thomas F. Cooney, H. Trey Skinner and S.M. Angel, *Appl. Spectrosc*. (in press).
43 Thomas F. Cooney, H. Trey Skinner and S.M. Angel, *Appl. Spectrosc*. (in press).
44 Design of a Cone-Penetrometer-Compatible Probe and Housing: the LLNL Raman Probe," S. Brown, F. P. Milanovich, K. Kyle, M. L. Myrick, UCRL-JC-132637 PREPRINT, December 9, 1998

Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site

Project ID: 70132

Dr. Ken O. Buesseler, Woods Hole Oceanographic Institute

Dr. John F. Wacker, Pacific Northwest National Laboratory

Research Objective

We suggest that there are gaps and inconsistencies in our understanding of actinide behavior in groundwater due to the widely varying properties of Pu from different sources and due to variations in sampling and analytical methodologies. It is our intent to sample across defined contaminant plumes at the Hanford Site for Pu and other actinides. Samples are collected using a "micro-purge" low pumping rate technique and directly separated into truly dissolved and colloidal size classes with an ultra-clean cross-flow filtration (CFF) system. Pu redox samples are separated immediately in the field and ancillary samples are also carefully collected for supporting organic and basic geochemical analyses. High sensitivity thermal ionization mass spectrometry (TIMS) is used to detect the Pu isotopes in all size and redox fractions, thus providing information not only on Pu concentrations but on the Pu source, which can strongly influence Pu speciation and mobility. The combination of these state-of-the-art procedures and the demonstrated care taken to process these samples ensures that the data represent the original in-situ speciation. The results of such a careful basic research program would: i) provide the basis for accurate modeling and prediction of actinide transport; ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/ groundwater zone, and iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwaters. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies.

Speciation and Structural Characterization of Plutonium and Actinide-Organic Complexes in Surface and Groundwaters

Project ID: 54683

K.O. Buesseler, Woods Hole Oceanographic Institution

M. Dai, Woods Hole Oceanographic Institution
D.J. Repeta, Woods Hole Oceanographic Institution

Research Objectives

Migration of plutonium in the environment is a major issue at several DOE sites. As such, fundamental data concerning the interactions between various chemical forms of plutonium with compounds in the environment are essential for predicting Pu's behavior in the aqueous environment. Our research has focused on two important DOE sites, namely the Savannah River Site (SRS) and the Hanford Site (HS). Earlier assumptions that contaminants would migrate very slowly in the vadose and groundwater zones have been demonstrated to be incorrect based upon findings of prior monitoring programs and independent review. At this point in time, extensive cleanup and stabilization programs are underway at many DOE sites. These important DOE activities are challenged by the immense scope of the cleanup and the overriding need for more streamlined and focused solutions to the cleanup problem. The results of our research program would:

i) provide the basis for accurate modeling and prediction of actinide transport;
ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/groundwater zone
iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwater. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies.

Research Progress and Implications

Our first project focused on the development and testing of appropriate sampling and analytical techniques to study the association of actinides with dissolved organic complexes in subsurface waters. Our ongoing project is designed for: (1) the determination of the speciation of plutonium and other actinides (Np, U) in groundwater at the 100 and 200 areas at the Hanford Site. This includes the separation of Pu into particulate, colloidal and <1 kilo-Dalton dissolved phases and the determination of redox states and isotopic composition in each fraction; (2) the characterization of groundwater colloids, which includes submicron-sized inorganic particles and organic macromolecules (3) the prediction of the rate of transport and fate of actinides in the groundwater of the Hanford Site using a three-phase (dissolved-colloid-particulate) model.

1) Development of sampling and analytical techniques

Technique development in the project included work on well sampling and field processing procedures, cross-flow filtration (CFF) for the collection of groundwater colloids, plutonium oxidation state separations, actinide analysis by thermal ionization mass spectrometry (TIMS), and methodologies for characterizing the organic constituents of groundwater colloids. We have made use of a "micro-purge", low pumping rate procedure for groundwater sampling and on site cross-

flow filtration (CFF) for the collection of groundwater colloids. The application of CFF to groundwater speciation studies requires considerable care to minimize the potential of colloid formation and/or redox shifts during sample processing. We have developed and tested a suite of procedures which include extensive flushing and CFF preconditioning steps, in order to minimize these artifacts. Our experience is that if such steps are not taken, colloid precipitation and contamination can occur. We also separated our ultrafiltration samples on site into oxidized and reduced fractions. This is done immediately in the field after sample collection under N_2 gas, which is crucial to minimize any alteration of ambient redox characteristics.

The high sensitivity of the TIMS facility at the Pacific Northwest National Laboratory (PNNL collaborative effort with Wacker/Kelley) has been extremely important to the success of all of our studies. Subfemtogram ($<10^{-15}$ g) detection limits are critical for following the far-field transport of Pu in the environment, and for determining Pu isotopic abundances in small subfractions of the total groundwater sample. TIMS is advantageous over more commonly used alpha-spectrometric techniques due to its higher sensitivity and its ability to quantify multiple Pu isotopes.

2) Results from Savannah River Site Seepage Basin F-Area

Our field study at SRS was focused on the F seepage basin area of SRS. Sampling was undertaken by following a groundwater plume downstream of the seepage basin as well as in a background monitoring well upstream from the basin. The F-area was one of two main sites where chemical separations facilities were located. We determined highly variable $^{240}Pu/^{239}Pu$ atom ratios (vs. the global fallout average of 0.18), with the most elevated values downstream. We attribute the highest $^{240}Pu/^{239}Pu$ ratios to samples that have been impacted by the decay of ^{244}Cm ($t^1/_2$ = 18.1 yr.) to ^{240}Pu in the seepage basin wastes. Redox speciation experiment shows that >75-95% of the ^{240}Pu is in an oxidized form. This supports the hypothesis that a unique ^{240}Pu rich source from the more mobile precursor ^{244}Cm, leads to enhanced mobility resulting in increased $^{240}Pu/^{239}Pu$ ratios downstream. A low $^{240}Pu/^{239}Pu$ ratio in the background well signifies a Pu source other than global fallout and is most likely due to weapons grade Pu waste of some local origin.

Most of the Pu at SRS is in the oxidized <1kD forms, which would be significantly more mobile than standard models predict. Size fractionation studies show only < 5% of the Pu as colloidal form, which is consistent with the higher oxidation states, and with overall low natural colloidal organic carbon levels at this site. In contrast to prior studies, we therefore conclude that colloids do not play a significant role in groundwater Pu transport at this site.

These findings suggest that Pu at SRS would be significantly more mobile than standard models predict.

3) Hanford 100-K sampling in March/April 1999

Comprehensive field sampling activities at the Hanford Site were completed March 22-April 6, 1999. Initial groundwater samples from wells near the 100 K reactor building indicate a local Pu source (see annual report in 1998). It was our intent to further define the plume and model Pu transport through comprehensive sampling activities. In addition to acquiring samples through the normally scheduled site sampling efforts at four groundwater wells (199-K-107A, K-28, K-30, and K-109A), we performed comprehensive sampling at four additional wells (199-K-27, K-32A, K-36, and K-110A).

During these comprehensive sampling activities, samples were processed on-site using an ultraclean cross-flow filtration (CFF) system. About 40 Pu isotopic composition samples, 50 Pu oxidation state samples (processed on-site), and 4 concentrated colloidal fractions were collected during this field effort along with other ancillary samples. A water sample was also taken from the Columbia river downstream of the 100-K area. Although the Pu levels in the groundwater at 100-K area are extremely low and would not pose a direct threat to the environment, it is important to know the migration potential of the contaminant into the Columbia River in order to establish the longer term risk assessment at this site. Processing of samples from this field work is in progress, and results will be presented at the EMSP national workshop in April, 2000.

Planned Activities

We are currently processing a large number of samples collected from the HS 100-K area. We are expecting to complete the bulk of the sample analysis and data processing during the first half of 2000. Based on the information, we will be conducting new field research at HS as detailed in the proposal. Our main focus remains on Pu speciation, mobility and the potential role that colloidal material may play in the Pu transport in groundwater.

Publications and presentations generated from this project

Dai, M., J.M. Kelley, K.O. Buesseler, R.A. Belastock, T.C. Maiti and J.F. Wacker (1998). Size fractionated Pu isotopes in the ocean, a pond and groundwater, AGU Spring meeting, May 1998, Boston, EOS, 79(17), pg.138.

Dai, M.H., J.M. Kelley, K.O. Buesseler, R.A. Belastock, T.C. Maiti and J.F. Wacker (1998). Size fractionated Pu isotopes in surface and subsurface waters, ACS/DOE EMSP workshop, July 27-30, Chicago.

Dai, M., J.M. Kelley, K.O. Buesseler et al. (1999). Isotopic composition, speciation and mobility of Pu in the groundwater at DOE Savannah River Site, AGU Spring meeting, May 1999, Boston.

Dai, M., K.O. Buesseler, J.M. Kelley, et al. (1999). Size fractionated Pu isotopes in a coastal environment, *J. Environmental Radioactivity* (accepted)

Repeta, D.J., T.M. Quan, L.I. Aluwihare and A. Accardi (1999) Dissolved organic matter in fresh and marine waters. Amer. Soc. Limnol. Oceanogr. Annual meeting, Santa Fe, N.M.

Buesseler, K.O., Dai, M. et al., (1999) Speciation, mobility and fate of actinides in the groundwater at the Hanford Site, EMSP PI workshop, Nov. 16-18, Hanford.

Information Access

Results from these EMSP projects can also be found at: http://cafethorium.whoi.edu