Subsurface Science Program

Co-Contaminant Chemistry Subprogram

Five-Year Plan of Basic Research

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Document Purpose

This document has been assembled for potential investigators and others who seek information on the goals, focus, scientific content, and anticipated accomplishments of the Co-Contaminant Chemistry (CCC) Subprogram. This 5-year plan (FY 1993-98) will be updated in FY 1996 to reflect substantive changes in direction or scope. A field research component to the subprogram is currently being planned that will be described in an addendum to this report.

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Preface

The U.S. Department of Energy (DOE) Office of Energy Research has long been a supporter of basic research on contaminant biogeochemistry in surface waters, soils, subsurface systems, and the marine environment. This research has led to fundamental advances in understanding how radionuclides, metals, and organic substances behave in natural systems, and in recognizing the important chemical, hydrologic, and biologic factors that control their mobilization and their transport. In 1989, the DOE/Office of Health and Environmental Research (OHER), Subsurface Science Program (SSP) accelerated research on the subsurface geochemical behavior of complex chemical contaminant mixtures. The accelerated research was motivated in part by DOE's need to remediate subsurface contamination at its many production facilities where nuclear processing, weapons development/testing, and waste disposal have occurred for more than 40 years. Countless waste sites exist at these facilities, and reports of subsurface contamination by mixtures of metals, radionuclides, and organic ligands have been frequent. The SSP, through the Co-Contaminant Chemistry Subprogram, is committed to the development of basic scientific information on the subsurface behavior of organic-radionuclide mixtures that can assist in the development of improved

models for transport predictions, new technologies for safe remediation of DOE lands, and protection of valuable groundwater resources nationwide.

This document formalizes DOE's plans for research on co-contaminant mixtures for the next 5 years. Research progress since 1989 has been significant, with emphasis placed on interfacial geochemistry, including adsorption, dissolution, and electron transfer reactions. However, the true complexities of the chemical, hydrologic, and microbiologic interactions controlling co-contaminant migration in the subsurface have become apparent during the course of research, demanding (1) focus on a limited suite of contaminant mixtures to assure comprehensive scientific advances and (2) realignment of research emphasis as described in this document. Since the initiation of this research in 1989, disposal costs for mixed organic-radioactive wastes have soared, more cases of subsurface contamination by radionuclides and organic substances have been reported on DOE lands, and DOE's remediation efforts have been challenged by complex scientific, technical, and political issues. Collectively, these events reinforce the need to continue co-contaminant chemistry research and to strengthen aspects where research opportunities and information needs appear greatest.

The DOE/SSP intends to embark on a new phase of co-contaminant chemistry research that emphasizes interdisciplinary research and multi-investigator experiments, placing greater focus on geomicrobiological phenomena, coupled process research (microbial effects on geochemistry, depositional/diagenetic effects on mineral distribution and contaminant retardation, etc.), and field scale issues. A scientific peer review in June 1994 was highly supportive of these proposed research directions. This office believes that inter-

disciplinary questions surrounding co-contaminant migration in the subsurface are the most significant scientific challenges facing DOE's remediation efforts and are those that, if resolved, will lead to the greatest advances in understanding the biogeochemical function of subsurface water systems. This document has been distributed to inform those who may be interested in the content of the research and DOE's future plans and to provide guidance to new investigators on research priorities.

Frank J. Wobber, Ph.D.
Program Manager
Subsurface Science Program

Introduction

Protection of groundwater resources is a national concern that requires a fundamental understanding of the geochemical behavior of inorganic and organic chemical mixtures in subsurface environments. This understanding must take into account the interactions among chemical, microbiological, and transport processes in heterogeneous geological materials that compose these environments (Figures 1 and 2). However, existing scientific information is insufficient for long-term predictions of the concentrations, bioavailability, and migration velocities of inorganic-organic contaminant mixtures in the vadose or saturated zones. Important scientific issues that limit predictions include the following.

- The identity, thermodynamics, and kinetics of multispecies geochemical reactions on mineral surfaces or on organic materials in subsurface sediments have not been documented well enough to formulate mechanistic models that predict the mobilization, retardation, or immobilization of contaminant mixtures.
- Simultaneous geochemical and microbial processes in subsurface environments induce complex synergistic or antagonistic interactions that affect how contaminant mixtures are transformed and transported. These processes and interactions have received inadequate research attention.
- Spatial heterogeneity in chemical, mineralogical, and physical properties, which are products of geological processes, has scale-dependent effects on geochemical reaction rates and magnitude that are inadequately understood.

These basic scientific issues are significant for DOE because during a period of many years inorganic and organic chemical agents were released to common disposal sites regardless of the potential environmental implications (Riley and Zachara, 1992).

Because of these releases, mixtures of radionuclides, metals, organic complexing agents, and organic solvents are found in subsoils and

Mixed chemical interactions can enhance or suppress contaminant migration and, as a result, will have a major impact on the success and viability of national remediation efforts.

groundwaters at DOE sites. Combinations of these and other contaminant classes that were mixed during disposal are now known to interact with each other through such reactions as aqueous complexation or cosolvation, thereby causing complex subsurface chemical behavior that is not well understood.

The interactions, which may be either direct or indirect, are termed "co-contaminant interactions." Mixed chemical interactions can enhance or suppress contaminant migration and, as a result, will have a major impact on the success and viability of national remediation efforts. Many co-contaminants are organic substances that may stimulate subsurface microbiologic activity. A firmer understanding of co-contaminant interactions in subsoils, geological media, and groundwater is critically needed and will contribute to resolving the complex subsurface contamination problems that exist at DOE sites (DOE 1990a, b).

Figure 1. Fluvial deposits of Pliocene age containing streambank gravels and overbank sands exposed in the White Bluffs near Hanford, Wash. Subsurface sediments typically exhibit complex stratigraphy and heterogeneity over various scales that impact solute migration. Chemical transport will vary significantly between the different lithologic zones as a result of contrasting water transmission and geochemical properties.

As part of OHER, the Subsurface Science Program has accelerated research in co-contaminant chemistry since 1989 in order to address fundamental scientific issues involved in the subsurface migration of contaminant mixtures. Research focuses on the behavior of organic-radionuclide mixtures because these are unique to DOE sites and because major questions about their subsurface biogeochemical behavior exist. The program stresses interdisciplinary research and multi-investigator collaborative experiments that target multicomponent geochemical reactions, their mediation by microorganisms, and factors governing their manifestation in natural subsurface environments.

Research in the Co-Contaminant Chemistry (CCC) Subprogram addresses the following general questions:

- Does aqueous complexation of a metal cation by an organic ligand invariably lead to enhanced mobility in unsaturated and saturated sediments? How do complexed metal or radionuclide ions sorb to mineral surfaces? What geochemical conditions enhance or suppress their reaction at the mineral-water interface?

Figure 2. Mineral reactants that impact contaminant behavior may show significant heterogeneity in distribution over sub-meter scales. Dark colored Fe-oxides show complex distribution paralleling depositional features in these Pliocene age fluvial sediments near Hanford, Wash. Determination of valid chemical reaction parameters for field-scale predictions requires explicit consideration of the distance scales over which key properties vary.

- How does dissolved or mineral-associated natural organic matter influence radionuclide stability, mobilization, and transport in subsurface environments?
- How does microbial degradation of complexing organic ligands affect metal mobility? How much do aqueous and surface complexation affect the biodegradation rate? Can microorganisms facilitate the valence cycling of polyvalent metal contaminants in subsurface environments, and does their activity modify the surface chemical reactivity of oxides and layer silicates?
- To what extent do depositional and postdepositional features such as bedding, fractures, and secondary mineral distributions control reactive co-contaminant transport in porous media? Are these features important to contaminant transport, and what averaging techniques or strategies are most appropriate at the field scale?

Scientific Opportunities

Accurately predicting the migration velocities of contaminants within subsurface environments is currently not possible because the geochemical and microbiologic processes determining concentrations, valence, and speciation are not sufficiently understood. Comprehension of linked interfacial/dissolution reactions and slow rate processes (abiotic and microbiologic) characteristic of subsurface environments is especially limited. Chemical mixtures complicate transport predictions because synergistic or antagonistic reactions (biotic and abiotic) among contaminant species may be the primary determinants of migration velocities. The nature, magnitude, and rates of such interactions are not well known.

Data bases, models, and process understanding relevant to individual contaminant suites, such as organic-radionuclide mixtures found at DOE sites, are also limited.

In subsurface environments, geochemical, microbiological, and hydrologic processes are coupled; that is, each one affects the other. An example is microorganisms that couple the oxidation of organic matter to the reduction of solid phase Fe(III) or Mn(IV) typically present in the form of oxide solids. This microbially mediated valence change affects the composition and aqueous speciation of groundwater, the mineralogy of grain coatings, and a variety of contaminant-solid reactions. The

The effects of coupled geochemical, microbiologic, and hydrologic processes are poorly understood.

implications of such process coupling are unknown and have received little attention from researchers. An inadequate understanding of process coupling is one of several reasons why predicting mixed contaminant migration in the subsurface is difficult at the present time.

Major research opportunities exist that emphasize organic-radionuclide mixtures and multidisciplinary questions:

- Interfacial processes, such as adsorption, dissolution, and surface-catalyzed abiotic and microbiologic reactions on natural mineral surfaces.
- Co-contaminant speciation measurements in groundwater and on subsurface mineral material.
- Microbial mediation of electron transfer reactions and organic ligand-metal complex behavior.
- Geochemical controls on contaminant bioavailability and transformation kinetics.
- Mass-transfer controls on biogeochemical reactions, including kinetics, mixing phenomena, nutrient/electron donor-acceptor dynamics, and the effects of mineralogical, geochemical, and physical heterogeneities.
- Influence of in situ mineralogical and geological features (grain coatings, phase associations) and structure (depositional and mineralogic features) on reaction rates, microbiologic phenomena, and co-contaminant retardation.
- Scaling mechanistic information on geochemical and microbiologic processes to the field.

Goals

The overall research goal of DOE's co-contaminant chemistry research is to establish a fundamental understanding of (1) the geochemical and microbiologic reactions that control aqueous concentrations and fluxes of organic-radionuclide mixtures in subsurface environments and (2) the factors controlling the magnitude and rates of these reactions at the field scale. As research progresses, new information on the interfacial and biogeochemical processes that control groundwater chemistry and chemical evolution will emerge, and improved reactive-transport models will be developed to use in forecasting the migration of complex contaminant mixtures.

Specific technical goals of the CCC Sub-program are summarized below.

- Identify the chemical nature (e.g., speciation and bonding) of metal-organic and radionuclide-organic ligand complexes on important subsurface mineral surfaces through direct spectroscopic interrogation that emphasizes uranium, plutonium, and cobalt.
- Determine the identity, kinetics, and thermodynamics of key geochemical and microbiologic reactions controlling the microscopic chemical behavior of organic-ligand complexes of Co, U, Pu, and selected metal cations in subsurface materials.
- Establish the role of microorganisms in mediating subsurface geochemical reactions of organic-metal complexes and modifying the reactive properties of mineral surfaces under conditions relevant to groundwater systems.

- Develop improved models to predict multicomponent equilibrium and kinetic reactions of organic-radionuclide mixtures in subsurface materials with and without water flow, and including microbiologic effects.
- Define the interrelationships among chemical, microbiological, and transport processes through the use of collaborative intermediate-scale flow cell¹ experiments with organic-inorganic mixtures and porous media with idealized mineralogic and physical heterogeneities.
- Establish spatial correlation functions between contaminant reactivity/retardation and reactive mineral distribution in representative field sites to develop strategies for prediction of contaminant reaction parameters in heterogeneous subsurface environments.

Long-term goals stress understanding of fundamental processes and mechanisms controlling contaminant behavior in groundwater systems.

¹ Intermediate-scale flow cells are meter-length (i.e., 1–2 m) experimental systems in which two-dimensional reactive transport experiments can be performed in homogeneous or heterogeneous porous media.

Research Scope and Content

The CCC Subprogram focuses on biogeochemical and contaminant transport processes that occur in natural field environments such as those shown in Figures 1, 2, and 3. Subsurface materials are physically, chemically, and biologically heterogeneous as a result of depositional and diagenetic processes and past/existing hydrologic conditions. Research is attempting to understand

complex co-contaminant surface reactions on natural materials from these environments, such as the natural Fe-oxide and smectite-coated sands shown in Figures 4 and 5. Investigations are also under way in the laboratory and at a field site to establish how the prominent subsurface structures shown in Figures 1, 2, and 3—such as lenses and stringers of sands, clays, and reactive metal oxyhydroxides—affect co-contaminant dispersion, retardation, and transport.

Figure 3. Outcrop of Atlantic Plain coastal sediments in Delaware containing bedded sands and gravels. Dark areas represent zones of Fe- and Mn-oxide accumulation that were deposited as a result of hydrologic and biogeochemical processes. The Fe- and Mn-oxide enriched layers are zones of enhanced contaminant reactivity (adsorption, oxidation) as a result of the coordinative properties of these oxide coatings. Similar stratigraphic features are common in the subsurface and strongly control reactive chemical transport. Describing contaminant migration through such zones with a heterogeneous distribution of reactants is a focus of the research.

Current research uses select contaminant mixtures found at DOE sites (Riley and Zachara, 1992)—emphasizing mixtures of metals or radionuclides with natural (humic substances, carboxylic acids) or anthropogenic (nitrilo-carboxylate) organic complexing agents used for decontamination activities or element specific separations in nuclear processing. (See the Appendix for a listing of contaminants found at DOE sites and those selected for research.) Furthermore, research that includes combinations of Co, U, or Pu with EDTA, NTA, oxalate, citrate, or humic substances (constituents that have been selected for collaborative research) receives priority. DOE intends to acquire a comprehensive understanding of the interactive subsurface behavior of these selected constituents because they represent a much broader suite of metals, radionuclides, and organic ligands found on DOE lands.

Research targets contaminant suites important at DOE sites including mixtures of metals and radionuclides with natural and anthropogenic organic complexing agents.

projects involve university and national laboratory participants and range in content from spectroscopic examination of chemical bonding in aqueous complexes, in solid phases, and on surfaces to investigations of coupled processes such as the transport and mobilization of chemical species in heterogeneous porous

The CCC Sub-program includes hypothesis-driven research on basic geochemical processes and their links with microbiology and hydrology. Data collection activities that are not tied to specific scientific hypotheses receive low priority. Existing

Figure 4. Sand grain isolated from Pleistocene age sediments of the Atlantic coastal plain at Oyster, Va. Light colored surface precipitates filling grain pits are crystalline Fe-oxides (goethite, ferrihydrite) that strongly bind both anionic and cationic contaminants. Researchers are investigating the surface chemistry and surface complexation properties of these oxides for radionuclides and radionuclide complexes, the kinetics of their dissolution and morphologic dependence, and the rates of mass transfer into their interstices.

media representative of subsurface environments (Figure 6). Selected project abstracts and literature citations follow this subprogram plan as examples of ongoing research.

As stated previously, DOE expects individual projects to be interactive rather than independent. As individual investigators address co-contaminant interactions from the molecular through the microscopic to the macroscopic scales, their combined research activities will yield (1) an understanding of biogeochemical reactions involving DOE

co-contaminants, (2) improved descriptive and/or predictive models incorporating microbiologic reactions and data bases representing DOE contaminants, and (3) insights on the coupled effects of microbiological and hydrologic processes on co-contaminant transport in the field. Given the multidisciplinary emphasis, the success of the subprogram requires integrating research results from individual projects and developing interactions linked through collaborative experiments. (See the Appendix.)

Figure 5. Sand grain from a subsurface water bearing zone near Hanford, Wash. Light patches are smectite particles that may strongly bind radionuclide cations such as UO_2^{2+} , or that may become destabilized/released by changes in aqueous chemistry to migrate as mobile colloids. Researchers are evaluating how mineralogic properties of smectites, such as layer charge and crystallite morphology, influence their reactivity toward metal ions and organically complexed radionuclides. Also, research is under way to characterize the effects of microbial reduction of structural iron in these solids on their surface charge properties and capacity to mediate electron transfer reactions.

Figure 6. Subprogram content: laboratory research.

Approach

The scientific approach for co-contaminant chemistry research is shown in Figure 7. Resolving the complex technical issues involved in the environmental behavior of DOE co-contaminants requires interdisciplinary research. Collaboration among investigators is encouraged, and multi-investigator experiments (see Appendix) focus research efforts on a common set of scientific hypotheses and research goals.

Researchers with complementary capabilities pool their expertise to resolve complex interdisciplinary hypotheses on co-contaminant behavior. The hypotheses center on interfacial geochemistry, reactive chemical transport, and biogeochemistry (microbial-geochemical interactions). (Figure 7) Collaborative experiments using batch systems and meter-scale flow cells (Figures 8 and 9) are planned for Co with EDTA, U with oxalate or citrate, and Pu with NTA. One or more multi-investigator field experiments are planned for later in the research period; initial geologic and geochemical characterization activities have begun at a site in Virginia. Collaborative research will provide unique comprehensive data sets on co-contaminant geochemistry and multidisciplinary insights on subsurface behavior. Examples of the multi-investigator research and rationale for its importance are provided in the Appendix.

To date, research within the CCC Subprogram has concentrated on laboratory investigations to resolve fundamental biogeochemical hypotheses. Model systems have been used to investigate reactions (i.e., aqueous complexation, adsorption, precipitation/dissolution, and transformation/degradation) and geomicrobiological phenomena controlling contaminant speciation and distribution between the aqueous and solid phases.

Researchers with complementary capabilities pool their expertise to test complex interdisciplinary hypotheses on co-contaminant behavior.

Representing natural groundwaters, aquifer solids, and microflora, these experimental paradigms have included suspensions containing electrolyte solutions, binary and ternary contaminant mixtures, single solid phases, and microbial isolates of known

function (Figure 10). Research with model systems has led to identifying the nature of solution and surface species, the scope and rate of specific geochemical or biogeochemical reactions, and the response of these reactions to changes in key variables. These models, which are based on relatively simple systems, have been applied to composite mineral materials from DOE sites and analog geochemical systems. Future research will emphasize resolving hypotheses related to the field scale by using intermediate-scale flow cells (Figures 8 and 9), undisturbed cores, and field studies.

Figure 7. Scientific approach of co-contaminant chemistry research.

Figure 8. Intermediate-scale flow cells, approximately 1–2m long and .25m wide, enable unique two-dimensional reactive transport experiments with relevant contact times and DOE contaminants. The flow cell shown here has inlet/solute injection ports on the left and a full array of sampling ports on the right to track solute migration and two-dimensional distribution. Intermediate-scale transport experiments are being used to test hypotheses related to mineralogic heterogeneities, subsurface microbiologic processes, and mass transfer between zones of different physical properties.

Subsurface materials and groundwaters are used to test hypotheses about controlling geochemical or microbiologic reactions and their kinetics and magnitude in mineralogically and geologically complex media. Research ranges from batch experiments with subsurface sediments or mineral components that vary in key properties to studies with undisturbed cores in which structural, depositional, and postdepositional features are preserved. Investigators are encouraged to use specimen solids and subsurface materials that have been assembled for co-contaminant chemistry research (Ainsworth and Zachara, 1989; Zachara and Smith, 1993). This collection contains subsurface materials that differ in content and chemistry of reactive components such as Fe-oxides, Al-oxides, layer silicates, calcium carbonate, and organic material and model or analogue materials (i.e., Fe- and Mn-oxide-coated sand) synthesized for controlled experiments.

A field experiment is planned to investigate coupled processes controlling the subsurface chemistry and transport of Co-EDTA or like complexes. A contaminated site on DOE lands will be used to (1) identify important in situ processes and their rates and (2) determine key subsurface properties and parameters governing complex stability and transport. Comprehensive information developed on abiotic and microbiologic reactions of Co-EDTA in laboratory studies and resulting linked biogeochemical transport models will provide a firm basis for field behavior interpretation. The field site, and companion laboratory studies, will also be used in formulating and testing new biogeochemical remediation strategies to enhance destabilization of the complex or to change its migration velocity for remedial purposes.

Figure 10. Association of Fe-reducing bacteria (strain B7; large dark rods) with acicular goethite (FeOOH) crystallites ranging from 0.1 to 0.5 μm in length. Bacterial exopolymer has been stained and has a dotted appearance in the photo. Research is under way to evaluate the susceptibility of subsurface Fe-oxides to bacterial reduction and the resulting effects on the surface properties of the solid and its contaminant retention/release properties. Different single cultures are being used to investigate the implications of bacterial Mn reduction/oxidation and organic ligand degradation on radionuclide geochemical behavior.

Figure 9. Intermediate-scale flow cells will be filled with undisturbed sediment blocks for future studies to investigate the impact of in situ mineralogic and depositional features on the transport and stability of organic-radionuclide complexes. Candidate sites for sediment block collection include sand and gravel pits in Worcester, Md. (photo), or Oyster, Va. (not shown).

Expected Results and Accomplishments

Co-contaminant chemistry research can be immediately applied to (1) understanding and predicting contaminant aqueous concentrations and transport in the vadose zone and groundwaters and (2) restoring contaminated subsurface environments at DOE sites. The anticipated results include the following:

- Basic scientific advances in understanding the nature of the bonding of metal, organic, and metal-organic complexes to mineral surfaces.
- Identification of dominant aqueous and surface species of key radionuclides and organic constituents under geochemical conditions common to the vadose and phreatic zones.
- Determination of the solid phases in subsurface materials with which contaminants associate over long contact times; improved understanding of the surface chemistry of natural oxides and clays and their interactions with organically complexed metals and radionuclides.
- Insights into the role of subsurface microorganisms in liberating organically complexed metals and radionuclides, modifying the surface chemical properties and reactivities of subsurface materials, and mediating the rates of geochemical reactions.
- Determination of the desorption or dissolution kinetics of chemicals from different contaminant associations to predict contaminant bioavailability and long-term release rates from contaminated subsurface materials.
- Description of the influence of mineralogic heterogeneities and depositional or structural features on co-contaminant mobility through geologic media.

Research will allow improved long-term predictions of mixed contaminant behavior at DOE sites and other sites nationwide.

Scientific and Industry Benefits

A comprehensive process-level understanding of the hydrology and biogeochemistry of organically complexed metals and radionuclides will emerge from this subprogram. Findings will be widely applicable to contaminated and pristine environments in which organic complexes of metals and radionuclides are the primary determinants of their subsurface mobility. Basic scientific progress will occur on (1) the mechanisms of bonding of metal complexes and organic ligands to mineral surfaces and (2) the interfacial chemistry of subsurface materials with applications to geochemistry, the environmental sciences, and industrial surface science. Surface spectroscopic techniques may be transferred to industry for analysis of the concentration and chemical form of trace species on heterogeneous inorganic and organic surfaces. Linked experiments with microbiology will provide insights into biological mediation of interfacial geochemical reactions in subsurface environments and fundamental relationships between mixed-contaminant geochemistry and microbiological nutrient cycling.

Subprogram research will also provide mechanistic knowledge for more accurate predictions of the subsurface behavior of chemical mixtures at DOE sites, helping to prioritize sites for cleanup and reduce environmental and health risks. Additionally, information on the biogeochemistry of subsurface environments and co-contaminant behavior may be transferred to industry for (1) selecting better restoration techniques,

Advanced measurement techniques and new biogeochemical concepts will assist government and industry efforts to remediate contaminated lands.

given new knowledge of contaminant types and subsurface chemistry; (2) evaluating the effectiveness of proposed remediation actions (e.g., well

placement and groundwater extraction rates); and (3) estimating the time required for contaminant removal from subsurface materials and groundwater.

Research results may also help industry develop new techniques to manipulate subsurface biogeochemistry to (1) increase rates of desorption or dissolution of solid-associated contaminants, thereby facilitating pump-and-treat methods; (2) retard mobile species, making treatment by excavation or vitrification more feasible; or (3) hasten beneficial abiotic or microbiological transformation or degradation reactions.

Program Documents

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Co-Contaminant Chemistry Subprogram

Representative Research Abstracts

DOE Laboratories Cited in the Representative Abstracts—

ANL	Argonne National Laboratory
BNL	Brookhaven National Laboratory
INEL	Idaho National Engineering Laboratory
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
ORNL	Oak Ridge National Laboratory
PNL	Pacific Northwest Laboratory

Research Abstract

Title

Chemistry and Microbiology Controlling
Chelated Radionuclide Transport

Principal Investigators

Harvey Bolton, Jr., and Don C. Girvin
Pacific Northwest Laboratory

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by providing a conceptual understanding of the adsorption/desorption of chelated radionuclides, the microbiological degradation of chelates, the speciation of the chelate and radionuclide during these processes, the influence of chelate adsorption/desorption processes on chelate biodegradation, and the effect of these processes on chelated radionuclide transport.

The investigators are collaborating with several projects in the subprogram on multi-investigator experiments concerning Co(II)/Co(III)-EDTA transport in intermediate-scale flow cells. Other principal investigators conducting these flow cell experiments include Dr. J.M. Zachara at PNL, Dr. P.M. Jardine at ORNL, and Dr. G.T. Yeh at Pennsylvania State University. This project is also conducting the research and taking responsibility for intermediate-scale flow cell experiments on the influence of sorption, aqueous speciation, and biodegradation on chelated radionuclide transport. These experiments will focus on Co(II)/Co(III)-EDTA transport and will involve collaboration with several investigators. They may include Dr. F. Brockman at PNL, Dr. A. Valocchi at the University of Illinois, Dr. B. Rittmann at Northwestern University, and Drs. Zachara, Jardine, and Yeh. The

investigators are collaborating with Dr. I. Rifai at LBL and Dr. D. Reed at ANL to investigate the influence of Pu-NTA degradation, Pu-NTA adsorption, and Pu-NTA adsorption-degradation interactions on plutonium speciation and solubility. Investigators are also working with Dr. Brockman to determine the form of NTA being degraded by the enzyme NTA mono-oxygenase.

Scope and Objectives

Depending on subsurface geochemical conditions, radionuclide transport in the subsurface environment is either increased or decreased when radionuclides are codisposed with synthetic chelating agents. In the presence of synthetic chelates, radionuclide-chelate complexes form, and the adsorption of this radionuclide-chelate complex by subsurface minerals is completely different from that of the radionuclide alone. Thus, the presence of synthetic chelates can either increase or decrease radionuclide mobility. The objectives of this project are to determine the surface chemical and microbiological properties that control the stability, persistence, and mobility of chelated radionuclides in subsurface environments. Batch and column experiments will be used to investigate the sorption/desorption behavior of cobalt, plutonium, and the chelating agents ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA) under varying geochemical conditions. Similarly, batch and column experiments will use subsurface sediments and chelate-degrading microorganisms to determine the rates of degradation for chelating agents and the geochemical/microbiological factors controlling these rates. Integrated studies of chemistry and microbiology will be performed in batch and columns and at the intermediate scale to

investigate chelate adsorption-biodegradation interactions and the influence of redox potential on the fate of chelated radionuclides.

The current limited scientific understanding of chelated radionuclide adsorption and biodegradation processes and of the physicochemical and microbiological parameters that influence these processes currently precludes assessment and prediction of radionuclide migration in the presence of synthetic chelating agents such as EDTA. Hence, it is unclear what subsurface environmental conditions enhance or inhibit chelated radionuclide transport and how geochemical/microbiological properties of the subsurface or waste environment can be manipulated to limit migration.

Accomplishments

This project and the research hypotheses being investigated focus on the subsurface physicochemical conditions influencing microbial transformations of synthetic chelates, adsorption of synthetic chelates and chelated radionuclides, and the mutual interactions of synthetic chelate adsorption and biodegradation upon one another. This research will allow DOE sites to (1) predict the persistence and movement of chelated radionuclides based on site-specific knowledge of microbial populations, groundwater geochemistry, and saturated zone lithology and hydrologic properties, and (2) develop effective site remediation.

Technology Transfer

The research conducted in this project provides DOE sites with useful information for understanding the geochemical and microbial processes that influence chelated radionuclide transport. Examples include (a) $^{60}\text{Co(III)}$ -EDTA adsorbs to aluminum oxide to a much lesser extent than $^{60}\text{Co(II)}$ -EDTA, indicating that subsurface conditions that enhance $^{60}\text{Co(III)}$ -EDTA formation (e.g., oxic Mn-oxide sediments) will result in enhanced ^{60}Co transport in oxide dominated sediments; and (b) the aqueous speciation of the chelate will influence its half-life in the environment. The chelate may complex predominantly groundwater or metal contaminants, with only a fraction chelating radionuclides such as ^{60}Co or ^{239}Pu . Knowing the major chelated metals and their effect on the half-life and adsorption of the chelate will provide information on the extent of chelated radionuclide transport.

Key Words

adsorption, biodegradation, chelate, radionuclide, subsurface transport

Research Abstract

Title

Chemical and Microbial Controls on the Fate and Transport of Co- and U-Organic Complexes in Subsurface Media

Principal Investigators

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Oak Ridge National Laboratory
Pacific Northwest Laboratory

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by providing an improved understanding and predictive capability of the basic chemical and interactive microbial processes that control the fate and transport of Co- and U-organic complexes in subsurface environments. Specifically, this project focuses on—

- Quantifying the time-dependent oxidation and sorption reactions of Co and U complexes with EDTA, citrate, and oxalate on mineral surfaces during transport.
- Establishing kinetic and mechanistic information on competitive microbial and geochemical reactions that control the fate of Co- and U-organic complexes during transport.
- Providing improved predictive capabilities of multispecies co-contaminant transport in heterogeneous subsurface media.

The investigators in this project are collaborating with:

- The University of Tennessee on contaminant and co-contaminant transport

issues in heterogeneous subsurface environments.

- PNL on the experimental and theoretical efforts concerned with Co-EDTA reactivity in subsurface environments.
- A working group of Co-Contaminant investigators involved in the design, interpretation, and prediction of Co-EDTA mobility in flow cells with controlled mineralogic heterogeneities consisting of Fe and Mn oxyhydroxides.

Scope and Objectives

The overall objective of this research is to provide improved insights on and predictive capabilities of coupled geochemical and microbial processes that control the fate and transport of co-contaminants in subsurface environments. Within the structure of the subprogram, this project focuses on the following specific investigations:

- (1) The kinetics and mechanisms of Co(II)EDTA²⁻ oxidation to Co(III)EDTA⁻ by subsurface Mn-oxides and mixed oxyhydroxides of Fe and Mn.
- (2) The geochemical processes controlling the fate and transport of EDTA chelated contaminants in heterogeneous, unsaturated subsurface environments.
- (3) The kinetics and mechanisms of U(VI)-citrate and U(VI)-oxalate sorption on morphologically distinct smectite clays during transport.
- (4) The effect of interfacial geochemical reactions, such as oxidation, sorption, and solid phase speciation, on the microbial reduction of Co- and U-organic complexes by Fe-reducing bacteria.

- (5) Improved theoretical capabilities for predicting the fate and transport of co-contaminants in heterogeneous subsurface environments.

The research is a combination of batch, multi-scale column transport, and intermediate-scale flow cell studies using Mn- and Fe-oxide coated SiO_2 and naturally heterogeneous porous media containing clays and oxyhydroxides of Fe and Mn. The kinetics and mechanisms of Co-EDTA and U-citrate/oxalate reactivity and oxidation are assessed as a function of (1) the pore water flux, (2) the initial co-contaminant concentration, (3) the dissolved O_2/CO_2 concentrations and residence times, (4) the aqueous concentration of surface reactive metals and pH, and (5) the presence of microbially mediated co-contaminant reduction reactions. The observed experimental efforts are numerically simulated with transport models developed to incorporate coupled time-dependent geochemical and microbial reaction mechanisms.

Accomplishments

To date, this project has significantly contributed to the current understanding of interfacial geochemical processes that control the fate and transport of EDTA chelated contaminants in subsurface environments. Some important scientific findings include:

- Experimental and theoretical evidence showing that subsurface Mn- and Fe-oxides catalyze the oxidation of Co(II)EDTA^{2-} to Co(III)EDTA^- . The rate of oxidation during transport was shown to be orders of magnitude more rapid in the presence of Mn-oxides, with time scales on the order of minutes to hours. The oxidation reaction was prevalent in both synthetic mineral systems and naturally heterogeneous subsurface systems. The consequence of the oxidation reaction was demonstrated by accelerated contaminant transport in the presence of the EDTA.
- Evidence documenting that, although subsurface Mn-oxides catalyzed the oxidation of Co(II)EDTA^{2-} to

Co(III)EDTA^- , a reversible loss in oxidative power of the mineral phase occurred during continuous reaction with the reductant Co(II)EDTA^{2-} . This demonstrated that the kinetics of Co(II)EDTA^{2-} oxidation to Co(III)EDTA^- was dependent on the rate of Mn-oxide surface regeneration, the latter being dependent upon the concentration and residence time of dissolved O_2 .

- Evidence indicating that the oxidation of Co(II)EDTA^{2-} to Co(III)EDTA^- in the presence of Fe-oxides was complicated by competitive time-dependent sorption reactions and solid phase-induced dissociation of some Co(II)EDTA^{2-} to form Fe(III)EDTA^- . In heterogeneous systems with mixed oxyhydroxides of Fe and Mn, the oxidation of Co(II)EDTA^{2-} to Co(III)EDTA^- was rapid and thermodynamically spontaneous, negating any competitive effects by subsurface Fe(III) for the EDTA ligand.

Technology Transfer

Results and data from this project have been transferred and applied to DOE site cleanup activities. The information generated by this research has been used by two private consulting firms involved in remediation efforts at numerous DOE sites at ORNL. They have utilized some of the data from this research to aid in the design of monitoring facilities associated with the restoration activities in the ORNL waste management area. The transport and geochemical parameters generated from this research are being used by these consulting firms and by the ORNL Environmental Restoration group to simulate the off-site transport of contaminants and co-contaminants from several waste storage areas at ORNL.

Key Words

Chelated-radionuclides, co-contaminant transport, mineral catalyzed oxidation, microbial reduction, kinetic transport modeling, competitive kinetic reactions

Research Abstract

Title

Co-Contaminant Chemistry at Interfaces

Principal Investigator

David E. Morris
Los Alamos National Laboratory

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by providing comprehensive information on the chemical nature of radionuclide surface complexes and the role that neutral-donor co-contaminants and simple organic ligands play in modifying the surface and exchange chemistry of these complexes. Such information is acutely needed for surface chemical equilibrium and transport models that are used to calculate aqueous concentrations in heterogeneous, sorbing porous media.

The investigators are collaborating with other subprogram participants at PNL, ANL, and LBL to devise and execute joint experiments pertaining to the subprogram's interfacial geochemistry hypothesis for sorption of radionuclides and their complexes with simple organic ligands. Additional collaborations have been initiated with these laboratories and ORNL to conduct intermediate-scale flow cell experiments.

Scope and Objectives

The focus of this project is on the surface sorption properties and the speciation of the sorption complexes of select radionuclides (uranium and plutonium) with and without organic co-contaminants, including the organic-soluble, neutral-donor ligand tributylphosphate and the simple, water-soluble organic ions oxalate and citrate. The soil substrates are 2:1 and 1:1 layered clay minerals such as smectites and kaolinites. Some of the specific issues that are being addressed are (1) the extent of uptake of radionuclides and ligands by the clays and subsequent alterations of clay structure; (2) numbers and types of binding sites in the clays; (3) specific binding modes (e.g., sorption to amphoteric edge sites versus exchange into fixed-charge sites, inner- versus outer-sphere sorption on edge sites, etc.) and the binding strengths for the radionuclides, the organics, and the radionuclide/organic complexes to the substrates; (4) influences of solvation/complexation on uptake and release of the radionuclides; (5) influences of surface complexation of metal ions and metal-organic complexes on subsequent hydrolysis of metals; and (6) effects of organic complexation and/or sorption on other (e.g., metal redox and organic transformation) chemical reactivity paths.

Accomplishments

These data will be useful to validate existing and emerging models of the surface complexation mechanisms and chemical reactivity of contaminants on environmental surfaces and interfaces. A systematic consideration of these issues will provide a framework for understanding and predicting the mobilization and transport of contaminants in the subsurface environment. This work may also enable the investigators to suggest improved remediation strategies based on chemical and/or physical intervention schemes. These results will also directly support the efforts of the newly formed Heterogeneity Working Group of the Subsurface Science Program. In particular, this work will produce results that address the Heterogeneity Working Group's hypothesis on how natural physical and chemical heterogeneities influence reactive chemical transport and chemical transformation and stability over space and time.

Technology Transfer

The potential for the transfer of the technology embodied in this project (data and data interpretation in this case) is excellent. The approach to characterization of surface complexation is inherently valuable to both DOE and industry in their respective efforts to remediate contaminated soils.

Key Words

clays, organic ligands, radionuclides, sorption, surface speciation

Research Abstract

Title

Radionuclide Speciation in
Groundwater Systems

Principal Investigator

Donald T. Reed
Argonne National Laboratory

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by establishing the aqueous speciation of radionuclides in the presence of organic contaminants, and more importantly, by establishing the interaction of these species with components of the subsurface environment. The results generated will improve both kinetic and thermodynamic data that are needed to model radionuclide speciation and will potentially lead to the development of new site remediation concepts.

The investigators are collaborating with Dr. H. Nitsche at LBL and with Dr. H. Bolton, Dr. D.C. Girvin, and Dr. J.M. Zachara at PNL in experiments to study the interactions of plutonium in multicomponent systems that include selected microbes, minerals, and cations in the presence of nitrilotriacetic acid. Collaborative efforts with Dr. A.J. Francis at BNL are also under way to investigate the interactions of Pu-citrate complexes with microbes that are known to degrade citrate. These collaborations, as a whole, will help establish the importance of the various subsurface processes in defining the geochemistry of plutonium-organic mixtures.

Scope and Objectives

The goal of this research is to define the predominant speciation (i.e., oxidation state, organic complexation, and aggregation) of plutonium and identify the key environmental factors that lead to its mobilization and immobilization in groundwater. Research questions being addressed include the following:

- Is the VI oxidation state of plutonium important in defining the near-surface geochemistry of plutonium-organic mixtures?
- What is the predominant oxidation state of plutonium in the presence of organic contaminants?
- What are the key interactions between plutonium organic complexes and microbes in the subsurface?

Future emphasis of the research will be plutonium-organic interactions in increasingly complex, i.e., more groundwater-relevant, systems. Greater emphasis will be placed on the lower oxidation states of plutonium, microbial interactions, cation competition, and mineral surface interactions. These studies will continue to utilize a combination of high-sensitivity laser techniques (photoacoustic and fluorescence spectroscopy), absorption spectrometry, potentiometric methods, and radiochemical counting methods to establish and monitor the aqueous speciation.

Accomplishments

The major accomplishments of this research project are (1) the completion of an extensive study of Pu(VI) hydrolysis in near-neutral systems, (2) an extension of photoacoustic spectroscopy to perform two-color photoacoustic detection of uranyl in aqueous media, (3) a completed study of Pu(VI)-citrate interactions at near-neutral pH, and (4) the initiation of microbial interaction studies with Pu(IV)-citrate complexes. Expected accomplishments include a more detailed understanding of the influence of microbes on plutonium-organic mixtures and the completion of plutonium speciation studies in real groundwater systems.

Technology Transfer

This research will potentially lead to two areas of technology transfer. The first is the development of improved in situ methods to detect actinides using laser-based techniques; this has applications to site characterization and on-line monitoring during waste treatment and remediation processes. The second is the development of remediation treatment concepts due to improved understanding of the geochemical and microbial processes that control the mobilization of plutonium-organic contaminant mixtures.

Key Words

migration, organic complexation,
plutonium, speciation, spectroscopy

Research Abstract

Title

Effects of Correlated Physical and Chemical Heterogeneities on Co-Contaminant Transport

Principal Investigator

Robert W. Smith
Idaho National Engineering Laboratory

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by determining the relationships between chemical and physical heterogeneities in oxide-coated subsurface sediments and by assessing how these heterogeneities affect the transport of uranium-citrate co-contaminant mixtures. The investigators are collaborating with Dr. J.M. Zachara and Dr. J.P. McKinley at PNL, Dr. D. Morris at LANL, and Dr. A.F.B. Thompson at LLNL. Drs. Zachara and McKinley are conducting static adsorption experiments to investigate the relative importance of edge sorption and ion exchange in the overall sorption of aqueous UO_2^{2+} organic ligand (oxalate and citrate) mixtures on natural subsurface materials. With the same materials, Dr. Morris is using direct spectroscopic interrogation to evaluate the specific surface complexation reactions that occur on mineral surfaces. This project extends

the investigation of the uranium system by considering the effects of transport on the sorption and speciation of uranium-organic ligand mixtures. It complements the strictly numerical investigation of Dr. Thompson on reactive transport in heterogeneous media by providing direct measures of the nature of the correlations between physical properties and chemical properties occurring at field scales.

Scope and Objectives

The principal scientific objectives of this research are to (1) determine the relationships between mineralogical and physical heterogeneity and the chemical reactivity of natural sediments, and (2) determine how the relationships between mineralogical and physical heterogeneity and the chemical reactivity of natural sediments affect the transport behavior of dissolved radionuclide-organic mixtures. Field, laboratory, and numerical research activities are being conducted to characterize a single outcrop for physical and hydraulic properties and to measure sediment reactivity using a combined cationic (UO_2^{2+})-anionic (citrate) chemical probe. Using intact core and observed correlations of properties, parallel numerical and column transport experiments will be conducted to evaluate the effect of correlated heterogeneities on the transport of UO_2^{2+} -citrate mixtures.

Accomplishments

Specific research accomplishments include (but are not limited to) (1) sorption constants for uranium on natural hydrous oxides; (2) relationships among permeability, grain properties, and porosity for sand and silt-sized particles; (3) relationships among permeability, porosity, and sorption for natural materials from a field site; and (4) improved capabilities to model the transport of co-contaminant mixtures in highly resolved heterogeneous systems. This information is essential to predict co-contaminant migration velocities and the time-dependent distribution of co-contaminants in the subsurface, both of which are required for in situ site remediation and risk/performance assessment activities at DOE contaminated sites.

Technology Transfer

Accurately predicting contaminant mobility in aquifers is important to the environmental restoration activities of DOE and private industry. This research enhances the accuracy of such predictions by defining how actual variability of aquifer physical and chemical properties influences transport; therefore, it is readily transferable to both DOE and private industry.

Key Words

heterogeneity, hydrous metal oxides, organic acids, sorption, uranium

Research Abstract

Title

Release of Oxide-Bound Toxic Metals by Naturally Occurring and Contaminant-Derived Compounds: The Role of Complexant, Reductant, and Adsorptive Characteristics

Principal Investigator

Alan T. Stone
The Johns Hopkins University

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by systematically examining how changes in the chemical nature and influx of natural or contaminant-derived organic compounds affect metal speciation and solubility. Quantitative information concerning complexation, reduction, and sorption processes generated by this project are used to improve the ability to predict metal speciation and the potential for migration at contaminated sites.

The investigators are collaborating with Dr. J.M. Zachara and other members of the subprogram on issues relating to complex interactions among chemical constituents in soils and aquifer sediments, and the speciation and reactivity of toxic metal contaminants.

Scope and Objectives

Organic compounds affect the extent of metal sorption onto subsurface solids by (1) competing with sorbed metals for available oxide surface sites, (2) forming metal-organic complexes in solution, (3) reducing metal oxidants to lower-valent forms with different particle-sorptive characteristics, and (4) dissolving the oxide phase through either reductive or nonreductive mechanisms. The objective of this work is to quantify these processes for typical subsurface organic compounds by paying close attention to reaction stoichiometry, equilibrium relationships, adsorption phenomena, and reaction kinetics and mechanisms. Emphasis is placed on subsurface environments where hydrous oxides of iron(III) and manganese(III,IV) are the predominant metal sorbent phases. Changes in the oxidation state, solubility, and speciation of cobalt (and uranium, in collaboration with the national laboratories) will be explored in relation to the complexant, reductant, and adsorptive characteristics of added organic constituents.

Mobilization via complexation is expected to be most effective when naturally occurring and contaminant-derived organic compounds have high capacities for binding "hard" (Co^{III} , U^{VI}), "borderline" (Co^{II}), or "soft" (Hg^{I} , Hg^{II} , Pb^{II}) toxic metal contaminants in comparison to dissolved (e.g., Ca^{2+} , Mg^{2+}) and solid (e.g., Al^{III} , Fe^{III}) ambient metal constituents. Organic compounds possessing reductant characteristics can affect metal mobilization directly, through reaction with the toxic metal constituent, or, indirectly, through reaction with host sorptive phases (e.g., $\text{MnO}_2(\text{s})$, $\text{FeOOH}(\text{s})$).

Accomplishments

An extensive examination of the release of $\text{MnO}_2(\text{s})$ -bound Co, Ni, and Cu by representative low molecular-weight organic reductants and complexants (e.g., hydroquinone, pyruvate, oxalate, and citrate) has been completed. The well-defined reaction chemistry exhibited by these compounds has made it possible to quantitatively discern between metal release via (1) metal-ligand complex formation in solution, (2) loss of available sorption sites through reductive dissolution of $\text{MnO}_2(\text{s})$, and (3) competitive sorption with Mn^{2+} released from the solid by reductive dissolution. Well-defined reaction chemistry also made it possible to highlight differences among the three metals. Co release is retarded by the formation of Co(III) on the $\text{MnO}_2(\text{s})$ surface. Ni release is inhibited by irreversible sorption into the $\text{MnO}_2(\text{s})$ lattice. Facile Cu release is observed; the extent of Cu release quickly reaches levels expected based upon equilibrium relationships.

Information gained from the experiments outlined previously has been used to quantitatively evaluate metal release mechanisms upon addition of natural organic matter from three southeastern swamps (including the Georgetown Site sample provided by Dr. J. McCarthy at ORNL) and two natural organic matter reference materials. Cu release from the $\text{MnO}_2(\text{s})$ surface was most sensitive to the complexant characteristics of each natural organic matter sample; Ni release was most sensitive to the reductant characteristics and to the extent of $\text{MnO}_2(\text{s})$ reductive dissolution. Various organic constituents within natural organic matter can either facilitate or inhibit metal release. Experiments have demonstrated that the adsorption of medium and high molecular weight organic compounds within natural organic matter samples inhibits approach $\text{MnO}_2(\text{s})$ reductive dissolution by oxalate and pyruvate, for example.

Toxic metal sorption onto $\text{FeOOH}(\text{s})$ is dominated by surface complex formation, while sorption onto $\text{MnO}_2(\text{s})$ is dominated by ion exchange into interlayer spaces and cavities. Toxic metal adsorption onto FeOOH has been examined at concentrations representative of near-field (5 to 300 M) and far-field (0.050 to 0.70 M) conditions. Available FeOOH surface areas exceed $25 \text{ m}^2/\text{L}$ in many subsurface environments. Fe(II) generated by FeOOH reductive dissolution must reach levels in excess of 1.0 mM in order for significant toxic metal desorption to occur. Experiments with representative low molecular-weight organic compounds have demonstrated that toxic metal complexation is a much more viable process for bringing about release from $\text{FeOOH}(\text{s})$.

Technology Transfer

Research results have great potential applicability to the restoration of soils and subsurface environments impacted by metal or radionuclide contamination. By advancing scientific understanding of the factors controlling metal ion desorption or dissolution rates, this research could provide the basis for new techniques to mobilize strongly bound metals or radionuclides from subsurface materials. Even at this early stage of research, this project has shown that aqueous geochemical variables can be manipulated to enhance metal release rates; information and insights derived from such observations are ready for application to DOE and other sites across the nation.

Key Words

adsorption, complexation, dissolution, metals, reduction

Research Abstract

Title

Application of Particle Methods to
Multicomponent Geochemical
Reactive Transport Problems

Principal Investigator

Andrew F.B. Tompson
Lawrence Livermore National Laboratory

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by providing a computational basis for examining the coupled impacts of flow, kinetic or equilibrium sorption reactions, and physical and chemical heterogeneity on mass transport in large subsurface formations.

The investigators are collaborating with other researchers in the subprogram who are determining reaction processes and rates associated with specific mineral/contaminant mixtures, and with scientists in the Heterogeneity Working Group engaged in characterizing material and property distributions in natural systems. In particular, plans to study uranium migration in near-surface sediments near a mining tailings facility in Utah are being developed.

Scope and Objectives

The objectives of this task are to develop, extend, apply, and integrate, as necessary, a highly resolved model of miscible contaminant migration and transformation phenomena within three-dimensional, nonuniform subsurface porous formations. The current numerical approach is based upon coupling a particle tracking (or Monte Carlo) transport algorithm with one or more simple reaction modules in an effort to build a tractable, computationally efficient simulator for use in large, detailed systems. Application emphasis currently involves equilibrium and kinetic sorption reaction phenomena, and will examine behavior in large, detailed systems in which non-uniform physical and chemical properties can be resolved. Experimental applications will initially focus on the behavior of idealized tracer and reactive compounds in synthetic systems in which spatially variable material characteristics are derived from idealized models of formation heterogeneity. Simulations will be used to (1) examine coupled behavior arising from physical and chemical process interactions; (2) validate the accuracy of "scaling" theories that predict effective rates of mass transfer, dispersion, and retardation; and (3) test or simulate the efficacy of heterogeneity-specific remediation schemes. Future collaborative applications will place more emphasis on behavior at specific field sites.

Accomplishments

Recent accomplishments include a series of simulations of fluid flow and chemical migration within highly resolved, three-dimensional regions with synthetically derived material properties. Nonuniformities in subsurface materials were represented as randomly correlated hydraulic conductivity and sorption partition coefficient fields. Four hypothetical contaminants were considered, one being inert and the other three independently obeying linear, Freundlich, and Langmuir partitioning relationships. Results showed distinct effects of the nonuniform flow and sorption processes on the overall displacement, dispersion, partitioning/retardation, and breakthrough behavior of the constituent plumes, as well as on the sharpening fronts and skewed concentration profiles associated with nonlinear partitioning models.

Future work will address kinetic and nonbinary sorption reactions, incorporate more realistic descriptions of heterogeneous property distributions, and focus on mass transfer or transformation processes induced by specific remediation techniques.

Technology Transfer

Mature portions of this work, including the numerical models and application methodology, may potentially be considered for transfer to private industry through technology transfer initiatives (TTIs) or cooperative research and development agreements (CRADAs) made between DOE, LLNL, other national laboratories, and specific industrial partners.

Key Words

reactive solute transport modeling,
physical and chemical heterogeneities

Research Abstract

Title

Subsurface Chemistry of Organic-Radionuclide Mixtures

Principal Investigator

John M. Zachara
Pacific Northwest Laboratories
with
John Westall
Oregon State University
James Leckie
Stanford University

Goals

This research is part of the Subsurface Science Program Co-Contaminant Chemistry Subprogram. It contributes to meeting the goals of the subprogram by—

- Determining the identity and kinetics of reactions on mineral surfaces and organic material controlling the migration velocities of organic complexes of Co and U in groundwater.
- Establishing the effects of selected microorganisms on the subsurface adsorption behavior and long-term stability of Co and U complexes with EDTA, citrate, and other ligands.
- Evaluating, in collaboration with others, the impact of mineralogic/chemical heterogeneities on the transport of Co and U organic complexes in disturbed and intact subsurface porous media.

The investigators in this project are collaborating with:

- LANL to establish the nature of uranyl surface complexes on smectite and other mineral phases using sensitive spectroscopies.

- Deep Microbiology investigators to determine the effects of Fe-reducing bacteria on the subsurface geochemistry of Co-EDTA and U-citrate complexes.
- A working group of Co-Contaminant investigators to perform intermediate scale flow cell experiments of Co-EDTA migration through porous media with heterogeneous distributions of Fe- and Mn-oxides.

Scope and Objectives

The overall objective of the research is to establish credible strategies to model the geochemical behavior (partitioning and transformation) of organically complexed radionuclides in mineralogically complex subsurface material. The goal is being satisfied through hypothesis driven laboratory research on abiotic and microbiologically mediated interfacial geochemical reactions using a series of subsurface materials, originating from DOE sites and other localities, that contain different surface reactive phases with varying morphologies and composition. The research involves (1) interaction experiments of complexed radionuclides with suspensions of natural material to establish adsorption magnitude, transformation kinetics, and reaction stoichiometry; (2) modeling to develop multi-reaction chemical models consistent with experiment; and (3) collaborative experiments with others to validate proposed reaction mechanisms by spectroscopy and flow cell experiments to investigate reactive transport under field relevant conditions. Central research questions include the following—

- How do surface complexation and ligand-promoted dissolution reactions couple to control the retardation and long-term stability of organic-radionuclide complexes in subsurface environments?
- Can Fe-reducing bacteria impact the adsorption behavior of organic-radionuclide complexes in subsurface environments by altering the surface morphology and surface chemistry of highly reactive Fe-oxide phases?
- How do heterogeneous in situ mineralogic features developed by the depositional process or secondary mineralization/diagenesis impact the reactive chemical transport of organic-radionuclide complexes?

Accomplishments

The project has made significant scientific contributions. Investigators have shown the geochemical conditions under which Co-EDTA complexes are adsorbed by subsurface materials, documented the important role of Mn-oxides in mobilizing Co as the Co(III)-EDTA complex, shown that retardation will change during transport as a result of Fe and Al dissolution promoted by the organic ligand, and developed an approach to model these complex reactions in subsurface materials. In collaboration with colleagues at LANL, investigators have developed a macroscopic, reaction-based chemical model for uranyl interactions with layer silicate clays that has been validated using luminescence and X-ray absorption spectroscopy. The model can describe and predict U adsorption and retardation in subsurface materials containing smectite sorbents. We have shown that Fe-reducing bacteria can utilize high surface area crystalline Fe-oxides from subsurface environments as a substrate and significantly influence their surface properties. Research is now proceeding to investigate their coupled effect on Co-EDTA and U(VI)-citrate adsorption chemistry.

Technology Transfer

This research is providing DOE and others with a sophisticated new understanding of how complexed radionuclides behave in subsurface environments. Approaches are being established to yield improved reaction-based models of adsorption and abiotic and biotic transformation processes to predict contaminant concentrations in subsurface environments. The research results and models will advance the accuracy of risk assessment, will allow rigorous analysis of restoration plans at both DOE and industrial sites, and will provide firm scientific concepts for development of new remediation techniques. Information from this project has already been used to assess factors controlling uranyl concentrations and mobility at two DOE facilities.

Key Words

adsorption, Fe-reducing bacteria, organic-radionuclide complexes, subsurface materials, surface chemistry, surface complexation modeling

Co-Contaminant Chemistry Subprogram

Appendix

Scientific Content,
Priority Contaminants, and
Collaborative Experiments

This appendix outlines a strategy to integrate research within the Co-Contaminant Chemistry (CCC) Subprogram, emphasizing (1) a set of priority metals, radionuclides, and ligands and (2) a series of collaborative experiments at the microscopic scale and intermediate scale that focus multi-investigator research on important scientific issues relevant to the DOE mission. Meeting the scientific needs of the subprogram requires the use of advanced measurement techniques and strong interdisciplinary research. A benefit of joint research will be the ability to integrate and rapidly translate research results from the molecular or microscopic scale to mesoscopic physical models that represent the natural subsurface environment.

Scientific Content

Research within the CCC Subprogram ranges from the molecular to the field scale (Figure 6) and includes three major activities:

- Spectroscopic studies for (1) determining the chemical identity of organic-radionuclide complexes in solution and on mineral surfaces and (2) establishing their bonding and structure as a basis for understanding microscopic reactivity.
- Interactive experiments with combinations of mineral solids, microbiologic isolates or single cultures, organic substances (alone and in combination), and single contaminants and mixtures for evaluating hypotheses about the identity, kinetics, and thermodynamics of important abiotic and microbiologic reactions in natural systems.
- Transport experiments that use not only columns of homogeneous porous media or undisturbed cores but also flow cells that simulate fundamental chemical and hydraulic properties of aquifers. These experiments will allow evaluation of hypotheses on the influences of mass

transfer and chemical kinetics, process coupling between chemistry and microbiology, and chemical/mineralogic heterogeneities. Research will begin to address field scale questions/scientific hypotheses after a suitable site is chosen.

Information exchange and scientific progress are served when a shared set of contaminant mixtures is selected for study. For example—

- The spectroscopic identification of surface complexes on mineral sorbents at the molecular scale can facilitate interpreting the interfacial behavior in mineralogically complex suspensions of subsurface materials.
- Thermodynamic constants and kinetic parameters that describe co-contaminant reactions in mineral and subsurface material suspensions can be used to quantify the contributions of geochemical and microbiologic reactions to multispecies transport in column and flow-cell experiments with water flux and chemical or mineralogic heterogeneities, and at field sites.
- Understanding how physical, biogeochemical, and microbiologic factors control the way geochemical reactions are manifested in undisturbed soil columns and cells with idealized heterogeneities can provide new insight on co-contaminant behavior in natural subsurface environments.

Because of the complex nature of chemical processing, testing, and research that has occurred at DOE facilities, numerous chemical mixtures are candidates for investigation (Figure 10, extracted from Riley and Zachara 1992). Priorities have been established because the financial resources within DOE are limited. Furthermore, the CCC Subprogram recognizes that some of these compounds and mixtures have already been studied by other agencies and does not intend to duplicate efforts. For

Figure 10. Generic chemical mixtures representative of contaminants on DOE sites.

Compound Class Mixture		Compound Class Components
Mixture 1		
chlorinated hydrocarbons	→	trichloroethylene, tetrachloroethylene, chloroform, carbon tetrachloride, chlorobenzene
with fuel hydrocarbons	→	toluene, benzene, ethylbenzene, cyclohexane
Mixture 2		
2a. cationic metals	→	Pb, Zn, Cu, Ba
with radionuclides	→	Th, U, Pu, Co, Cs/Sr
2b. anionic metals	→	CrO ₄ , AsO ₃ /AsO ₄ , CN, F
with radionuclides	→	TcO ₄
Mixture 3		
chlorinated hydrocarbons	→	trichloroethylene, tetrachloroethylene
or fuel hydrocarbons	→	toluene, benzene
or ketones	→	acetone, methyl ethyl ketone
with PCBs	→	Arochlor 1248
Mixture 4		
metals	→	Pb, Cr(III), Cr(VI)
or radionuclides	→	U, Pu, Co
with organic acids	→	oxalic, citric, formic, phthalic
Mixture 5		
metals	→	Pb, Hg
or radionuclides	→	U, Pu, Co
with complexing agents	→	EDTA, DTPA, NTA, tributyl-phosphate
Mixture 6		
metals	→	Pb, Hg
or radionuclides	→	U, Cs/Sr
with ketones	→	acetone, methyl ethyl ketone, methyl isobutyl ketone
Mixture 7		
metals or radionuclides	→	Pb, Co, U, Pu
with organic acids or complexing agents	→	EDTA, oxalate/citrate, tributyl-phosphate
with ketones or chlorinated hydrocarbons	→	acetone, trichloroethylene
Mixture 8		
metals or radionuclides	→	Pb, Co, U, Pu
with natural organic substances	→	humic and fulvic substances, low-molecular-weight organic acids

example, the U.S. Environmental Protection Agency (EPA) and the Electric Power Research Institute (EPRI) have extensively researched chlorinated hydrocarbons, fuel hydrocarbons, and PCBs (Mixtures 1 and 3).

Therefore, within the CCC Subprogram, DOE research focuses on those mixtures for which there are (1) long-term opportunities for fundamental research and (2) major environmental concerns centering on DOE sites. For this reason, the subprogram emphasizes mixtures of radionuclides with organic complexing agents, organic solvents, and natural organic substances (i.e., Mixtures 4, 5, 6, 7, and 8; Figure 10). The existence of organic/radionuclide mixtures as subsurface contaminants is a pressing problem at DOE sites, and the chemical interactions that occur in these mixtures are insufficiently understood.

Within the broad category of organic-radionuclide interactions, the mixtures must be further ranked. Specific contaminants are selected for research to allow development of an information base that can be integrated from the molecular through the microscopic and macroscopic scales. Using this integrated information base, researchers can predict co-contaminant behavior at the macroscopic, mesoscopic, and field scales, thus achieving a subprogram goal. The radionuclides, organic ligands, and solvents for which research is most justified and most urgent—given their co-contaminant reactions and frequency of occurrence on DOE lands—are summarized in Figure 11.

Collaborative Experiments

Multi-investigator experiments complement, but do not replace, the research of individual investigators. Collaborative experiments provide focal points for individual research; they also allow integration of efforts and findings. The following separate groups of investigators are collaborating:

- The interfacial processes group evaluates hypotheses related to complexation and electron transfer (abiotic and microbiologically mediated) reactions on natural surfaces.
- The biogeochemistry group investigates linked microbiologic-geochemical phenomena controlling the chemical speciation, stability, and reactivity of organic-radionuclide complexes in subsurface environments.
- The transport group integrates research across the microscopic, macroscopic, and mesoscopic scales by testing hypotheses on the migration behavior of co-contaminant mixtures in porous media with chemical/mineralogic heterogeneities and microbial activity.

Preliminary experiments being considered by the three groups are described below. The information does not include detailed experimental designs or comprehensive descriptions of experimental series that may be carried out in the future as these tend to be evolutionary. Additional collaborative

Figure 11. Priority chemical constituents that are the focus of co-contaminant chemistry research.

Radionuclides	Organic Ligands	Organic Solvents
Co (II and III) U (IV and VI) Pu (IV, V, and VI) Am (III)	EDTA, NTA, Oxalate Citrate Tributylphosphate Humic Substances	CCl ₄ Acetone Kerosene Methylisobutylketone

activities will be developed around a field study site, possibly in conjunction with another OHER/SSP subprogram or a DOE remedial site. Exploratory investigations that may lead to selection of a CCC field site began in FY 1994. Selected examples that illustrate the nature of the collaborative laboratory experiments are described below.

Interfacial Geochemistry

A collaborative experiment based on an interfacial chemical hypothesis that is currently under way is shown in Figure 12. This experiment revolves around the hypothesis that the retardation of UO_2^{2+} -organic ligand complexes (i.e., UO_2^{2+} -oxalate, UO_2^{2+} -citrate) in smectitic geologic material depends on the strength and quantity of surface complexes formed between the uranium aqueous complex (UL) and alumina sites (AlOH) on the edges of the smectite crystallites. Uranium is one of the most ubiquitous subsurface contaminants on DOE lands. Its subsurface migration is facilitated by complexation with organic ligands, but the surface chemical interactions of UL complexes responsible for retardation have not been established.

The hypothesis may be tested by investigating the sorption behavior of selected U-organic ligand complexes over ranges in pH, ionic strength, electrolyte cation valence, and $\text{CO}_2(\text{g})$ pressure in laboratory suspensions of natural smectites that vary in their crystallite morphology and edge surface area. These experiments are being performed by investigators familiar with both the mineralogy, reactivity, and microscopic surface chemical properties of layer silicates and geochemical models for calculating aqueous and surface speciation.

Collaboration involves chemical spectroscopists who directly measure the identity and concentration fraction of solution and surface species in a common model system. Spectroscopy can identify the surface reactions responsible for both the microscopic sorption behavior and the reaction stoichiometry

between aqueous species and the mineral surface, validating reaction based surface chemical models. Furthermore, molecular spectroscopy can determine the surface configuration and bonding of co-contaminant complexes, thus facilitating the interpretation of kinetic behavior and thermodynamic properties of co-contaminant complexes on the surfaces of natural mineral materials.

Biogeochemistry

Multi-investigator studies for the biogeochemical hypothesis are evaluating the influence of microbial activity on the subsurface geochemical behavior of organic ligand-radionuclide complexes. Research is investigating the microbial valence cycling of polyvalent radionuclides such as Co(II,III) -EDTA and the implications of organic ligand degradation on the aqueous speciation and adsorption chemistry of Pu-NTA. Collaboration between microbiologists and geochemists is focused on issues such as the influence of (1) adsorption of radionuclide complexes on the degradation rate of the organic ligand and (2) Fe-reducing bacteria on the surface chemistry of sorbing Fe-oxides and their destabilization/reduction of radionuclide complexes by enzymatic activity or ferrous iron release.

As an example, the Pu-NTA system is being investigated by a group composed of a microbiologist, a spectroscopist/radiochemist, and a surface chemist, among others. A simple to complex approach is being employed with parallel-biotic and abiotic experiments to investigate how the chemistry of Pu (as Pu-NTA) changes as the organic ligand is degraded by microorganisms. Studies are proceeding from spectroscopic studies of Pu-organic ligand complexation reactions to experiments of NTA degradation rates in presence of Pu and competitive cations and finally on to complex systems containing Pu-NTA, microbes, and reactive mineral surfaces.

Initial experiments will utilize a microbe that is known to degrade NTA (*Pseudomonas* strain ATCC 29600). Experimental issues to be

Figure 12. Example of collaborative experiment focused on uranium interaction with clay minerals.

Hypothesis

Retardation of U-complexes in smectitic geologic material is dependent on strength and quantity of edge coordination complexes (i.e., AIO-UL).

Materials

Natural smectites from DOE sites varying in particle size and crystallite morphology (i.e., face-to-edge ratio).

Experiments/Data

addressed include biosorption and uptake of plutonium, biotic valence transformation, and the effect of Pu on the mineralization of NTA.

This work revolves around the hypothesis that the generation of the Pu polymer (formed when the NTA complexant is removed) is proportional to the NTA mineralization rate.

Over the longer term, more complex systems will be investigated. Cations typical of groundwater environments such as Ca^{2+} , Al^{3+} , and $\text{Fe}^{2+/3+}$ will be systematically added to investigate the cations' ability to compete with plutonium for NTA, yielding NTA complexes with different degradation rates and liberating Pu as polymer. The increased uncertainty about the speciation of the various components will require more detailed supporting investigations. Complex experiments involving Pu-NTA, microbes, and solid surfaces will be initiated as a simple microcosm of the subsurface environment. It is hypothesized that adsorption of complexed Pu and ligand-promoted dissolution of the solid will profoundly influence the microbial degradation rate of NTA and the geochemistry of Pu.

Investigating the complex technical issues associated with these multicomponent microbiological-geochemical experiments will help establish the crucial factors in the mobilization and immobilization of radionuclide-contaminant mixtures in the subsurface environment. Furthermore, these collaborative experiments will establish a link between subsurface microbial ecology (i.e., functionality and activity) and contaminant geochemistry, a critical factor that has generally been ignored in studies of subsurface environments.

Reactive Transport

Collaborative experiments will use meter-long, intermediate-scale flow cells (Streile et al. 1987) and undisturbed cores of subsurface sediments. These experimental systems simulate different types of geologic, mineralogic, and chemical heterogeneities

that influence chemical species transport, including—

- Stringers of iron and manganese oxides, calcite, and organic material.
- Oxidized and reduced geochemical zones.
- Sedimentary structures, including clay lenses and cross bedding.
- Preferential flow paths and unique mineralogic coatings that have developed in situ from the interaction of chemical, hydrologic, and microbiologic processes.
- Clay, sand, and gravel interbeds; sediments with textural and mineralogic variations.

Intermediate-scale flow cells will be used to investigate both the effects of idealized physical and chemical heterogeneities and the influence of localized zones of microbiological activity. The flow cells allow two-dimensional reactive transport experiments with contact times representative of subsurface environments. Results from column experiments of undisturbed subsurface sediments will complement the information obtained. Collaboration among geologists, surface chemists, microbiologists, soil physicists, and hydrologists is a prerequisite to integrating data on geochemical reactions in static systems (e.g., reaction identity and equilibrium constants, kinetic parameters for certain reactions, and chemical models) with data on multispecies chemical transport observed in complex porous media.

A multi-investigator experiment based on the impact of mineralogic heterogeneity on the migration behavior of an organic-radionuclide mixture (Co^{2+} complexed by EDTA) is depicted in Figure 13. Complexes of ^{60}Co with EDTA have been identified as mobile subsurface constituents originating from waste sites at several defense related facilities. Laboratory observations that Fe-oxides represent the

Figure 13. Example of collaborative experiment focused on Co-EDTA migration through mineralogically heterogeneous porous media.

Hypothesis

Genesis of Co^{3+} -EDTA at oxidizing surfaces will—

- Increase apparent hydrodynamic dispersion of Co-EDTA.
- Generate asymmetric migration velocities/breakthrough profiles as a result of the differing sorption of the Co^{3+} and Co^{2+} species.

Materials

Fe and Fe/Mn-oxide stringers in micaceous sand that simulates stratified deposits commonly observed in subsurface materials.

Experiments/Data

prominent subsurface sorbents of anionic metal complexes and that Mn-oxides will oxidize Co^{2+} to Co^{3+} in EDTA complexes provide further scientific basis for this experiment. Using a two-dimensional flow field containing a heterogeneous distribution of Fe-oxide and mixed Fe/Mn-oxides, the experiment hypotheses are—

- Enhanced dispersion of Co-EDTA will result from the formation of a mixed $\text{Co}^{2+}/\text{Co}^{3+}$ EDTA population at oxidizing surfaces.
- The breakthrough of Co will be highly asymmetric because of (1) the different sorption of the Co^{2+} and Co^{3+} EDTA complexes (Co^{2+} -EDTA is more strongly sorbed) and (2) the dissociation of the Co^{2+} -EDTA complex to yield Al(III)-EDTA, Fe(III)-EDTA, and Co^{2+} through solid-phase dissolution.

These hypotheses can be evaluated in a meter-long flow cell containing stringers of Fe and Fe/Mn-oxides in sand, representing conditions often found in subsurface sediments and groundwater zones. Nonreactive tracers will be used to distinguish the hydrodynamic characteristics of the cell, including diffusivity into the oxide stringers. Cobalt(II)-EDTA will be injected into the flow cell along with the nonreactive tracer; Co^{2+} , Co^{3+} , Fe^{3+} , Al^{3+} , and EDTA concentrations will then be measured throughout the flow cell and in the effluent. The collaboration of geochemists, hydrologists, and others will show how mineralogic heterogeneity affects the kinetics and magnitude of geochemical reactions as well as their spatial manifestation within a contaminant plume in groundwater.

To satisfy long-term objectives of the CCC Subprogram, additional collaborative transport experiments with microbiologically active zones and undisturbed natural materials are required to determine the influences of depositional and structural features of the porous media, secondary mineral formation, and flow-path/microbiologic heterogeneity.

Contaminants

The following subset of chemical contaminants from Figure 11 has been selected for collaborative research:

- Co with EDTA, NTA, and/or humic substances.
- U with EDTA, citrate, or oxalate.
- Pu with EDTA, NTA, or citrate.
- U complexed with tributylphosphate in CCl_4 .

These mixed chemical or co-contaminant pairs represent important mixtures on DOE lands and are, therefore, excellent candidates for research. Their subsurface behavior is complex; nevertheless, well-defined collaborative research will improve macroscopic and field scale predictions. Other mixtures may later be added to this list of priorities depending on research results and ongoing characterization activities at DOE sites.

A tentative schedule for multi-investigator experiments that address the three hypotheses areas is shown in Figure 14. This schedule simply identifies plausible near-term research targets. The plan will evolve as (1) the scientific contributions of the early collaborative experiments become apparent and (2) the field research component becomes defined.

The experiments begin with single-contaminant systems that focus on one dominant process. They quickly progress to contaminant mixtures and the effects of interacting processes (chemistry, microbiology, hydrology) as more information evolves from individual projects. The scope and anticipated benefits of the multi-investigator experiments are summarized in Figures 15, 16, and 17. The later experiments—especially those involving microbiology—are interdisciplinary and have broader bases in both scope and science. These experiments will involve participants from the CCC and other Subprograms of the Subsurface Science Program.

Figure 14. Tentative schedule of collaborative experiments.

Figure 15. Scope and benefits of multi-investigator interface geochemistry experiments.

<p>SCOPE Integrate surface sensitive molecular spectroscopies with microscopic/macroscopic experimentation to facilitate understanding of chemical reactions on mineral surfaces and organic materials responsible for co-contaminant retardation in subsurface environments.</p>	
<p>EXPERIMENT</p>	<p>BENEFITS</p>
1. U—no complexants.	Establish surface reactions responsible for UO_2^{2+} adsorption on natural surfaces dominated by smectites and Fe-oxides.
2. U—with organic acid complexants.	<p>a) Determine which aqueous complexes are adsorbing and their probable surface bonding environment.</p> <p>b) Clarify competitive interactions with Al^{3+} and Fe^{3+} (for the organic ligand) and CO_3^{2-} (for UO_2^{2+}), and the resulting effects on UO_2^{2+} interfacial behavior.</p>
3. Pu—with inorganic ligands in groundwater.	Identify surface chemical reactivity of specific aqueous species of Pu.
4. Pu—with organic and inorganic ligands.	Investigate organically mediated valence transformations and their impact on speciation and adsorption.

Concluding Remarks

A series of collaborative experiments that take advantage of the multidisciplinary expertise in the CCC Subprogram has been identified and will be expanded when a field site is chosen for the subprogram. These experiments will function as focal points for individual research; they also integrate scientific results from different measurement scales up to that of the natural subsurface environment. There is unparalleled opportunity for rapid application of new findings at the molecular and microscopic scales and better

interpretation of biogeochemical reactivity and transport behavior in experimental systems representative of groundwater zones. By focusing research on select contaminant mixtures prevalent at DOE sites, the scientific progress made will have broad implications for other radionuclides, metals, organic ligands, and geochemical environments. Fundamental scientific advances in the understanding of the biogeochemistry of contaminant mixtures in heterogeneous domains are expected to greatly improve the ability to predict migration and to remediate contamination in groundwater zones.

Figure 16. Scope and benefits of multi-investigator biogeochemistry experiments.

SCOPE	Establish the role of microorganisms in controlling the stability and valence of organic-radionuclide complexes in subsurface environments.	
EXPERIMENT	BENEFITS	
<p>1. Co with EDTA and—</p> <p>a) Fe-oxides and Fe-reducing bacteria.</p> <p>b) Subsurface materials containing Fe-oxides of differing morphology and size and Fe-reducing bacteria.</p> <p>c) Mn-oxides, subsurface sediments, and Mn(II) oxidizing bacteria.</p>	<p>a) Establish the effects of Fe-reducing bacteria on the surface chemistry of sorbing Fe-oxides and the stability of the Co-EDTA complex as Fe^{2+} concentrations increase.</p> <p>b) Determine effects of sorption site heterogeneity on the kinetics of Co-EDTA dissociation during bacterial Fe-reduction in subsurface materials.</p> <p>c) Determine whether Mn-oxidizing bacteria catalyze Co(II) EDTA oxidation by regeneration of Mn(IV)-oxide surfaces.</p>	
<p>2. Pu and NTA with—</p> <p>a) Ligand degrading microbes.</p> <p>b) Microbes and Al-oxides.</p>	<p>a) Investigate the rates of Pu polymer formation during the microbial degradation of NTA associated with the Pu-NTA complex.</p> <p>b) Establish the role of adsorption of the Pu-NTA complex on its destabilization/disassociation during the course of NTA biodegradation.</p>	
<p>3. UO_2 with Fe-reducing bacteria and smectites.</p>	<p>Identify whether microbiologically reduced Fe in ferruginous smectites can function as a reductant for aqueous and surface associated UO_2, and establish the reduction kinetics.</p>	

Figure 17. Scope and benefits of multi-investigator transport experiments.*

SCOPE Determine the influence of chemical and mineralogic heterogeneities and the interactive effects of microbiology on the transport of organically complexed radionuclides.	
EXPERIMENT	BENEFITS
1. Co with—	
a) EDTA and Fe- and Mn-oxides.	a) Understand kinetic effects of Co(II)-EDTA oxidation and competitive respeciation with Fe(III) via solid phase dissolution.
b) EDTA and Fe(III)-reducing bacteria.	b) Establish the influence of spatially heterogeneous microbial redox cycling on co-contaminant migration profiles.
c) EDTA in undisturbed subsurface materials with Fe- or Mn-oxide stringers.	c) Investigate influence of "real world" Fe- and Mn-oxide coatings, mixed Fe/Mn- oxide phases, and flow path heterogeneities on Co(II)/Co(III)-EDTA oxidation kinetics and reactive transport.
2. U with—	Flow Cell
a) Organic acid complexants.	a) Understand factors controlling U-valence and plume development in a two-dimensional flow field containing spatially heterogeneous sorbent domains.
b) Organic acid ligands and microbes.	b) Understand factors controlling U-valence and plume development in a two-dimensional flow field containing microbial Fe(III) reduction and organic ligand biodegradation.

* A field transport experiment series is under planning and will be attached to this document at a later date. An existing project is investigating the influence of the spatial distribution of Fe-oxides in a field outcrop on the sorption properties of the outcrop materials for UO_2^{2+} and UO_2^{2+} -citrate complexes.

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