Research Accomplishments

FOR THE

Environmental Management Science Program

FY2001 Year-End Summary

Published November 2001

U.S. Department of Energy
Office of Environmental Management
Office of Science

COVER GRAPHIC: Dr. Paul P. Woskov, Massachusetts Institute of Technology, along with his co-principal investigators Dr. T. Bond Calloway Jr, Savannah River Technology Center, and Dr. S. Kamakshi Sundaram, Pacific Nothwest National Laboratory, has received a R&D 100 Award for his work on the Millimeter-Wave Measurements of High Level and Low Activity Glass Melts. The device uses coherent millimeter waves to measure the viscosity of high temperature melts. The viscosity is a very important property in the creation of high-level and low-activity glass waste forms. Precise control of the viscosity is necessary to provide the proper pouring parameters, proper mixing of the contaminants and the glass matrix and extending melter refractory lifetime. This device has a greater viscosity measurement range than its competitors, is more accurate, and can withstand higher temperatures. It will also have applications outside the EM Program [see Project #81897, renewal of #65435].

EXECUTIVE SUMMARY

The Environmental Management Science Program (EMSP) was established by Congress in 1996 under the Department of Energy (DOE) Environmental Management (EM) Office of Science and Technology to "develop and fund a targeted long-term basic research program that will result in transformational or breakthrough approaches for solving the Department's environmental problems." The EMSP is a partnership between the Department of Energy (DOE) Office of Basic and Applied Research and the Office of Science, and funds competitively awarded research that seeks scientific understanding leading to reduced remediation risks, costs, or schedules, and helping to solve currently intractable problems. As such, EMSP supports research that leads directly to the fulfillment of the following EMSP research objectives:

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

- "Bridge the gap" between broad fundamental research that has wide-ranging applicability such as that performed in DOE's Office of Science and needs-driven applied technology development that is conducted in EM's Office of Science and Technology

- Focus the nation's science infrastructure on critical DOE environmental management problems.

The intent of this *EMSP Research Accomplishments Summary* is to provide information concerning varied research transition activities. Research transitions are measures of how successfully the program has transitioned knowledge gained from research projects to other areas. These measures may be in the form of actual transfers of new knowledge or data gained through research products or processes to other areas within EM, such as Focus Areas and Crosscutting Programs, or may be more general knowledge transfer measures found in similar research programs, such as collaborations, numbers of student researchers, peer reviewed papers and presentations (communication products), or consultations.

Since 1996, the EMSP has funded over 300 basic research projects at 90 universities, 13 national laboratories, and 22 other governmental and private laboratories in 39 states and 7 countries. Many of these projects have generated sufficient technical data and identified specific, potential field applications to warrant movement into the applied R&D arena. Research accomplishments from EMSP-funded projects, with total quantities in each category as follows:

Collaborations	*Total*
Consulting - provide advice or technical expertise	46
Joint interaction - researcher/end-user in joint interaction	49
Mission directed - project direction provided by end-user	19
Program interaction - researcher to researcher interaction	60

• *Student Researchers*	*Total*
Undergraduate Researchers	103
Master Researchers	260
Ph.D. Researchers	69
Post Doctoral Researchers	184

• *Research Transfers*	*Total*
Commercializations	13
Deployments	10
Field Tests	15
Focus Areas & Crosscutting Programs	3
Processes	2

The information presented in this document is an attempt to capture research transition activities as of October 31, 2001, and therefore should not be considered to be a complete or accurate listing. Research publications and other communications products for EMSP-funded projects are documented in *Communication Products for the Environmental Management Science Program*.

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Introduction

RESEARCH ACCOMPLISHMENTS FOR THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

INTRODUCTION

The Environmental Management Science Program (EMSP) is a partnership between the Department of Energy (DOE) Office of Basic and Applied Research and the Office of Science. The mission of the EMSP is to develop and fund a targeted long-term basic research program that will result in transformational or breakthrough approaches for solving the Department's environmental problems. The EMSP funds competitively awarded research that seeks scientific understanding leading to reduced remediation risks, costs, or schedules, and helping to solve currently intractable problems. The sites will use the understanding gained through EMSP-supported research to improve their cleanup efforts. Implementing these approaches will lead to reductions in cleanup costs, as well as reductions in risks to workers and the public. The Environmental Management Science Program (EMSP) has funded over 300 basic research projects at 90 universities, 13 national laboratories, and 22 other governmental and private laboratories in 39 states and 7 countries.

Many EMSP projects have generated sufficient technical data and identified specific, potential field applications to warrant movement into the applied R&D arena. Based on the technical strength of his work for Project #81897 (renewal of #64535), *Millimeter-Wave Measurements of High Level and Low Activity Glass Melts*, Dr. Paul P. Woskov, Massachusetts Instutite of Technology, has received an R&D 100 Award for the creation of a new device that uses coherent millimeter waves to measure the viscosity of high temperature melts. Viscosity is an important property in the creation of high-level and low activity glass waste forms. This device has a greater viscosity measurement range than its competitors, is more accurate, and can withstand higher temperatures. It has a broad range of applications in non-EM Programs as well (see cover photo).

The information contained in this document has been gathered from various sources, such as interactions with EMSP staff, proceedings from EMSP workshops and technical conferences, principal investigators, the Project Tracking System, EMSP Project Annual Reports, and literature searches. The information presented is an attempt to capture research transition activities and therefore should not be considered to be a complete or accurate listing. This document contains the best available data as of October 31, 2001.

Problem Areas Addressed by EMSP Research

The EMSP focuses on the key EM problem areas defined in the *EM Research and Development Program Plan*. These problem areas are grouped by waste area, representing the scope of cleanup facing EM. These areas are the basis for developing science and technology investments. The focus areas link both research and technology development to these eight problem areas:

- *Deactivation and Decommissioning* research advances science to solve environmental problems associated with placing equipment and structures in a desired end state. Desired end states include complete removal and remediation of the facility, release of the facility for unrestricted use, or release of the facility for restricted use.

- *High-Level Waste* research advances science to solve environmental problems associated with storage tanks containing highly radioactive wastes, which include organic and inorganic chemical compounds in solid, colloidal, slurry, and liquid phases.

- *Mixed Low-Level Waste (MLLW) /Transuranic Waste (TRU)* research advances science to solve environmental problems associated with very limited treatment options and disposal capacities.

- *Nuclear Materials* research advances science to solve environmental problems associated with unstable materials, such as plutonium metals and oxides, highly enriched uranium and nuclides of other actinide elements, and the long-term storage of stabilized materials.

- *Spent Nuclear Fuel* research advances science to solve environmental problems associated with safely and efficiently managing spent nuclear fuel from both domestic and foreign reactors.

- *Subsurface Contamination* research can assist the Department in solving environmental problems associated with hazardous and radioactive contaminants in soil and groundwater that exist throughout the DOE complex, including radionuclides, heavy metals, and dense, nonaqueous phase liquids.

- *Health, Ecology, and Risk* is a crosscutting problem area; therefore, the research investment will impact cleanup work across the Department of Energy (DOE) complex. There is scientific uncertainty about the levels of risk to human health and the environment at the end stages of the DOE cleanup effort. Accurate risk analyses require thorough knowledge of contaminant characteristics, basic ecological processes and principles, rates at which contaminants move through ecosystems, and health and ecological effects. In particular, better knowledge of radionuclide and toxic chemical transport dynamics and the potential effects of long-term exposure to low levels of radionuclides, in combination with other contaminants, is needed to assist the DOE in its efforts to protect the public, workers, and the environment. This research would also improve the understanding of threatened and damaged ecosystems and processes to restore their viability and quality.

- *Long-Term Stewardship* research supports issues that impact the Department in assessing site conditions after a site is closed and a remedy has been implemented. Long-term stewardship research is necessary to support the Department's commitment to protect human health and the environment after site closure for sites where cleanup to levels acceptable for unrestricted use is not possible.

Science Categories

EMSP research is classified further within each problem area based upon the type of science being conducted. Science classifications include the following:

- Actinide Chemistry including uranium, americium, and plutonium
- Analytical Chemistry and Instrumentation includes sensor development and diagnostics such as non-destructive examination
- Biogeochemistry studies such as oxidation/reduction and biological degradation
- Engineering Science research such as robotics and remote sensing
- Geochemistry that focuses on reactions within the subsurface
- Geophysics that included advanced characterization methods
- Health Science research on dose assessment, bio-markers, and risk estimates
- Hydrogeology that targets subsurface transport mechanisms and predictive modeling
- Inorganic Chemistry including tank waste speciation and metals remediation
- Low Dose Radiation to understand the health effects of low doses of radiation
- Materials Science which studies phenomena such as corrosion, glasses and other waste forms
- Microbial Science research on areas such as bio-remediation and microbial transport
- Plant Science area such as phytoremediation
- Separations Chemistry that focuses on high level tank waste treatment alternatives.

DOCUMENT LAYOUT

Research transition activities are addressed in three accomplishments categories: collaborations, research transfers, and student research. In addition, this volume contains sections covering success posters, fact sheets, and workshops sponsored by the EMSP. Project publications are documented in *Communication Products for the Environmental Management Science Program*.

1. *Success Posters.* These highlight several projects that are examples of EMSP research being integrated into EM cleanup. Some of these projects have been deployed at DOE sites to support cleanup while others are still in the maturation process but are closely linked to site needs.

2. *Fact Sheets.* These are summaries of EMSP projects or groups of projects linked to specific problem areas within EM. The fact sheets highlight program efforts to support EM cleanup.

3. *Collaborations.* This section reports the collaborative effort being undertaken by EMSP projects to further research and to transfer research towards technical maturity. To date, 159 collaborations have been reported.

4. *Research Transfers.* The main objective of EMSP-funded research is to address EM clean-up needs through 2070. This section highlights 32 research transfers (i.e., deployments, products, spin-off business, field tests, continuation by others, etc.) by project. Some activities listed in this section may be planned actions and are provided to ensure follow-up contacts are made.

5. *Graduate Students.* One of the two main objectives of the EMSP is to develop a cadre of environmental scientists to meet 21st century clean-up needs. This section tracks the impact the EMSP is having on increasing the cadre of environmental researchers. The number of Post Doctoral, PhD, Masters, and Undergraduate students are reported by EMSP project. Graduate student researcher's names are noted where provided. As of March 30, 2001, 525 undergraduate, graduate, and post graduate researchers are funded under this program.

6. *TopicalWorkshops.* This is an overview of the various workshops sponsored by the EMSP to promote research integration and transfer. This includes the EMSP National Workshops, site-specific workshops focusing on a specific site such as the one hosted by the Idaho National Engineering and Environmental Laboratory (INEEL), and topical workshops such as the vadose zone series of workshops held at Hanford or the long term monitoring workshop held at INEEL.

EMSP-funded research activities are listed within each section by EMSP Problem Area and Science Category, and include the project number, title, name of the principal investigator, and a brief description of the respective project. Transitions between Problem Areas are indicated by oversized, bold text on a shaded background, with associated science categories appearing as bold text preceded by a shaded horizontal rule, as follows.

EMSP Problem Area

EMSP Science Category

Photos and illustrations are placed throughout the document to coincide with information regarding the EMSP research project to which they apply.

Success Posters

Success Posters

Success Posters address a problem area wherein a suite of technologies provides a solution to the problem, but are sometimes used for technology solution topics. This section includes seven Success Posters created by the EMSP to support National Workshops and various other presentations nationwide.

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Science Advancing Solutions

for Deactivation and Decommissioning

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

Principal Investigator:
Greg Collins
Naval Research Lab

Project Number:
64982

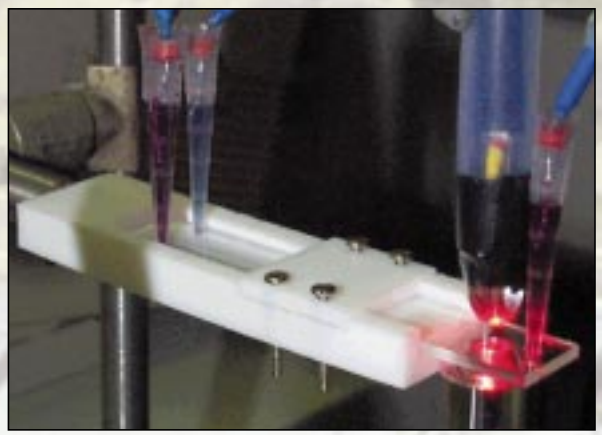
Science Category:
Analytical Chemistry & Instrumentation

Value to EM Cleanup:

- Quantification and identification of radionuclides and heavy metals, e.g., U, Pu, Cs, Sr, Hg, and Pb.
- Field portable for in-situ characterization.
- Rapid separation times, e.g., uranium characterized in less than a minute.
- Low volumes of secondary waste
- Low equipment cost.
- Low analysis cost

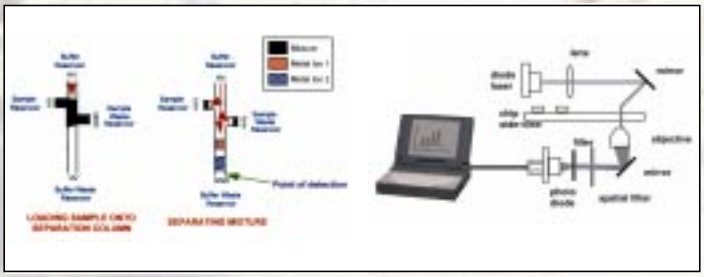
Accomplishments:

- Synthesis and purification of four, new fluorescence-tagged metal complexation ligands-cyclen, crown ether, iminodiacetic acid, and calix[6]arene.
- Demonstrated separation and quantitation of uranium on a microchip in less than a minute.
- Highly selective ligands or matrix components have been established for uranium detection
- Both absorbance and fluorescence detection modes have been demonstrated as sensitive modes of operation (ppb level detection limits) for uranium on a microchip.



Voltage is applied to the four reservoirs to transport ions and liquid down the microchannels.

Lab-on-a-chip showing microchannels and reservoirs



Through a process of electroosmosis and careful selection of applied voltages, metal on complexes are separated and identified by their differences in migration.

EMSP

For additional information visit the EMSP Website at
http://emsp.em.doe.gov

Environmental Management Science Program

Science Advancing Solutions

for Subsurface Contamination

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

Principal Investigator:
Frederick Colwell,
Idaho National Engineering and Environmental Laboratory

Project Number:
55416

Science Category:
Microbial Science

Value to EM Cleanup:

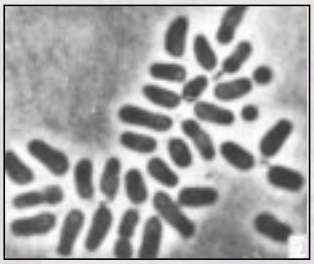
- The multi-level sampler provides an understanding of the chemical and microbiological conditions at specific vertical locations in the subsurface.
- A better understanding of subsurface chemical and microbial conditions helps identify potential in situ treatment solutions, and verify treatment effectiveness.
- Provides a necessary tool for evaluation of natural attenuation as a treatment alternative.

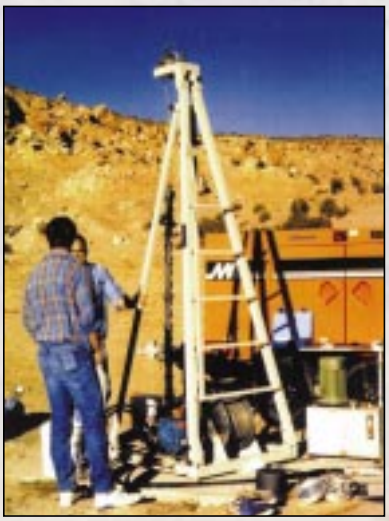
Accomplishments:

- Performed aseptic subsurface sampling in support of Test Area North (TAN) cleanup activities at the INEEL. Information used to establish protocols for enhanced in situ bioremediation.
- Determined the broad distribution of naturally occurring TCE-degrading microorganisms in the larger dissolved phase contaminant plume at TAN.
- Verified the presence of dissolved methane, a nutrient needed to sustain TCE-degrading microbes, in the Snake River Plain Aquifer at TAN, thus supporting a natural attenuation alternative in the proposed Record of Decision.

Aseptic sampling of fractured rock

Naturally-occurring TCE-degrading microorganisms may naturally attenuate the TAN TCE plume at low concentrations





Understanding the chemical and microbial conditions in the subsurface helps identify potential treatment solutions

EMSP For additional information visit the EMSP Website at http://emsp.em.doe.gov

Environmental Management Science Program

Science Advancing Solutions

for Subsurface Contamination

Design and Development of a New Hybrid Spectroelectrochemical Sensor

Co-Investigators:

William R. Heineman,
Carl. J. Seliskar,
Thomas H. Ridgway,
University of Cincinnati

Samuel A. Bryan,
Timothy L. Hubler,
Pacific Northwest National Laboratory

Project Number:
70010

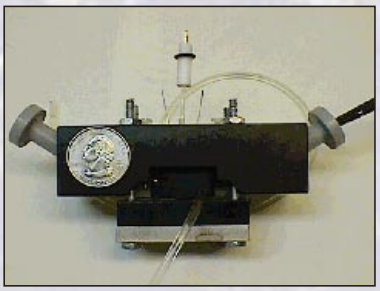
Science Category:
Analytical Chemistry and Instrumentation

Value to EM

- Aid in the characterization of complex waste material associated with DOE site cleanup
- On-site monitoring of collected and prepared samples for field evaluation
- Enhanced selectivity over currently available conventional sensors
- Monitoring of subsurface water and vadose zone

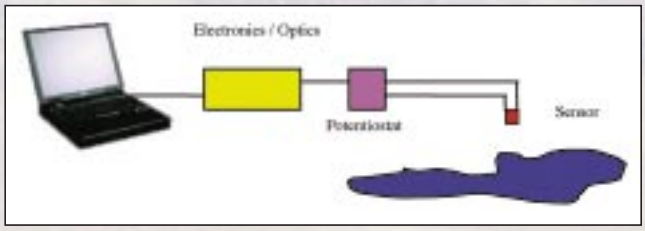
Accomplishments

- Concept demonstrated with detection of ferrocyanide, $Re(DMPE)_3^+$, $Ru(bipy)_3^{2+}$, and methyl viologen
- Selectivity against direct interferences demonstrated
- Signal averaging to achieve lower detection limits demonstrated
- Prototype instrumentation package to control electrochemical modulation and optical readout developed
- Sensor for detection of ferrocyanide in Hanford U-Plant 2 simulant solution demonstrated
- Sensor package (microcell and instrumentation) for demonstration on ferrocyanide in waste tank sample at Hanford developed
- This sensor has been successfully tested on technecium at concentrations ranging from 1-1,000ppm and has the possibility of being modified to detect other groundwater contaminants



This prototype sensor has a sample volume of 800 µl. The blue LED provides a simple light source and the working electrode consists of an indium tin oxide slide coated with a charge selective film.

The Virtual Software interface for spectro-electrochemical sensor allows for remote control of sensors and remote monitoring of sensor response.



Remote sensing can be achieved with the use of a portable computer connected to the cell through a module housing the electronics for data acquisition.

Science Advancing Solutions

for Deactivation and Decommissioning

TRU Decontamination with Plasma Etching

Principal Investigator:
Dr. Robert F. Hicks,
UCLA

Project Number:
54914

Science Category:
Materials Science

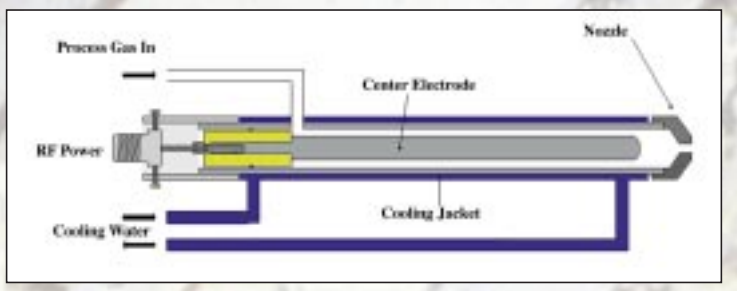
Value to EM Cleanup:

- Decontamination of TRU contaminated waste
- Low-pressure Low-temperature operation
- Cleaning rate of 1/2 ft^2/minute
- Low operating cost <$5/$ft^2$
- Low capital equipment cost <$100K
- No secondary waste
- Field Mobile

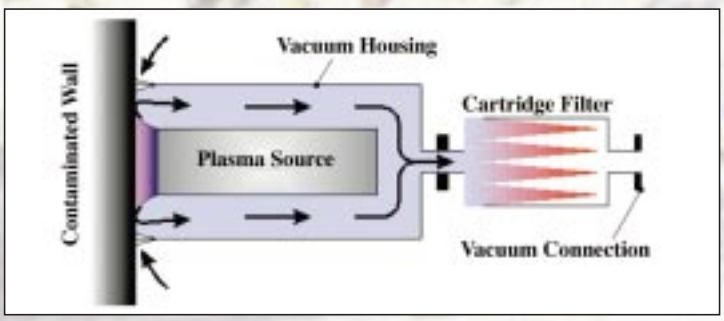
Accomplishments:

- We have demonstrated removal rates of tantalum, a surrogate for plutonium, in excess of 6.0µ/min.
- Vast improvements in the operability and reliability of the plasma source have been made.
- We have scaled up the source from a reactive beam area of 1.0 cm^2 to over 1.0 ft^2
- We have characterized the physics and chemistry of the atmospheric-pressure plasma jet: it generates $10^{11}cm^{-3}$ of ions and $10^{15}cm^{-3}$ of reactive neutral species.
- We have identified the surface chemistry of heavy metal etching: the rate is controlled by surface reactions between adsorbed F atoms and a metal fluoride layer.

4" wide decontamination nozzle



Schematic of Atmospheric-Pressure Plasma Decontamination Technology



Conceptual of TRU contaminant collection system

EMSP For additional information visit the EMSP Website at http://emsp.em.doe.gov

Environmental Management Science Program

Science Advancing Solutions

for Subsurface Contamination

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

Principal Investigator:
Dr. Ernest L. Majer,
Lawrence Berkeley National Laboratory

Project Number:
55264

Science Category:
Microbial Transport

Value to EM Cleanup:

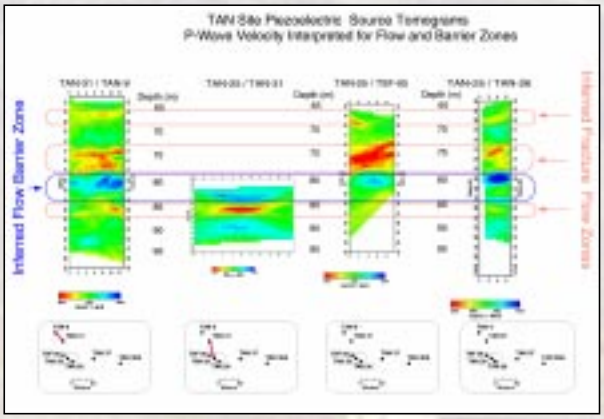
- Provides a cost-effective method for delineating the volume and distribution of highly contaminated fracture zones.
- Can be used to focus remediation efforts, estimate the duration of the remediation effort and to modify the conceptual model for implementing restoration at contaminated sites.

Accomplishments:

- Seismic Crosshole Tomography was successfully employed to image the subsurface between several ground water extraction and monitoring wells at the INEEL Test Area North (TAN)
- Low velocity zones delineated by seismic tomography correlate to fractured intervals known to contain elevated levels of 137Cs and 60Co.
- High velocity zones correlate to intervals of dense basalt with significantly lower concentrations of radionuclides.

Seismic recording van and receiver well with tripod

Sensors being checked for contamination



Seismic velocity tomograms show correlation between fractured flow zones and contamination.

EMSP For additional information visit the EMSP Website at http://emsp.em.doe.gov

Environmental Management Science Program

Science Advancing Solutions

for Deactivation and Decommissioning

D&D in Virtual Reality: A near-real-time, semi-autonomous virtualization modeling and imaging system to facilitate tele-operated D&D activities

Principal Investigator:
Dr. Robert J. Schalkoff,
Clemson University

Project Number:
55052

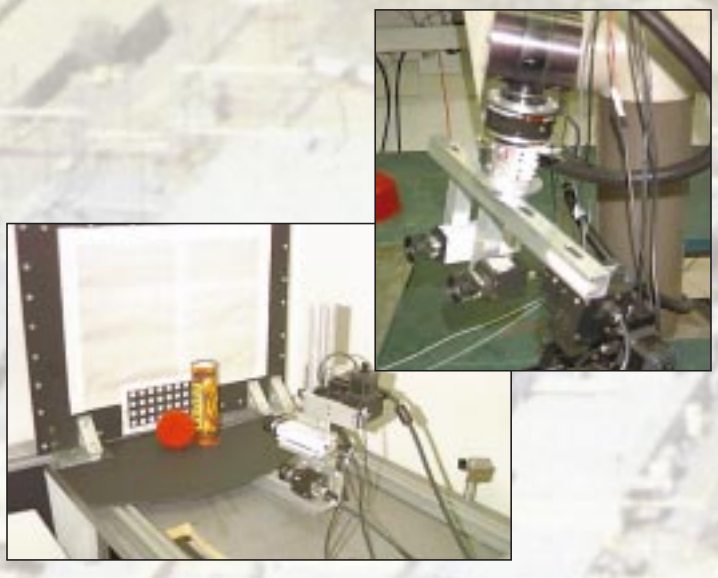
Science Category:
Engineering Science

Value to EM Cleanup:

- 3-dimensional model for Project Planning and Visualization.
- Virtual world operator training.
- Collision avoidance and tele-robotic guidance.
- Waste Packaging and handling optimization
- Reduces worker exposures in hazardous environments.

Accomplishments:

- A fourth generation vision sensing head has been built and tested
- The project is in the process of integrating the imaging system, the Virtual Reality rendering, and the robotics system, into a single operating unit.
- Negotiations are underway to locate a site for phase one testing of the integrated system under more realistic field conditions. The INEEL has expressed an interest in testing at their site in support of the DDROPS.
- Other parties outside the DOE have expressed interest in more refined development of the system.



Laser and camera setup during one of the initial system tests demonstrating the compact size of the scanners.

Image scanning system mounted on robotic arm for remote operations

EMSP For additional information visit the EMSP Website at http://emsp.em.doe.gov

Environmental Management Science Program

Science Advancing Solutions

for Subsurface Contamination

Microcantilever Sensors

Principal Investigator:
Thomas G. Thundat
Oak Ridge National Laboratory

Project Number:
60197

Science Category:
Analytical Chemistry and Instrumentation

Value to EM Cleanup:

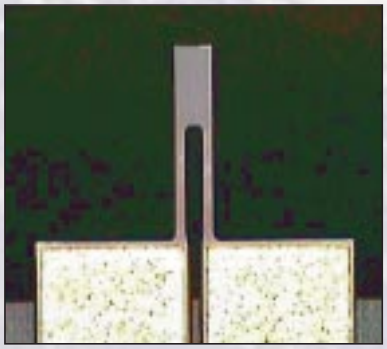
- Basis for real-time, portable, low-cost sensors for remediation and characterization.
- Single platform for chemical, physical, and radiological characterization of ground water and mixed waste.
- Identification of analytes with sub ppb sensitivity.

Advantages:

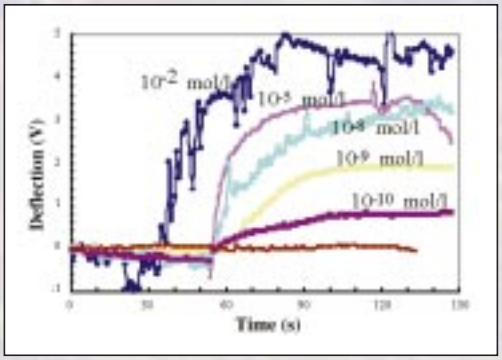
- Operates in solution.
- High sensitivity and selectivity.
- Single platform for physical, chemical, and radiological detection.
- No tagants or labeling necessary.
- Miniature and consumes less power.
- Can be micromachined and mass produced.

Accomplishments:

- Demonstrated detection of Cs^+ with 10^{-12}M sensitivity (dynamic range 10^{-2} - 10^{-12}M). Detected CrO_4^{2-}, Pb, Na^+, and K^+ ions.
- Detected alpha particles.
- Detected Cs^+ in tank waste simulant with high concentration of Na^+ and K^+ ions
- Demonstrated pH detection with high sensitivity (10^{-3} pH units).
- Detection of VOCs such as benzene.

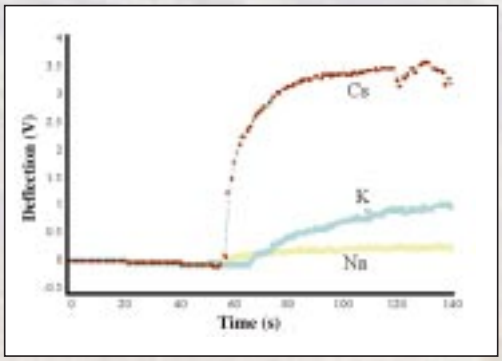


Optical image of a 180µm long silicon mirocrocantilever.



Microcantilever deflection as a function of Cs^+ ion concentration.

Microcantilever bending response for 10^{-5}M solutions of Cs^+, K^+, and Na^+



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Environmental Management Science Program

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FACT SHEETS

This section includes Fact Sheets highlighting EMSP Science Categories and associated Work Packages. These Fact Sheets were selected as part of an evaluation that focused primarily on the projects in the EMSP portfolio that were in more mature stages of development.

The Facts Sheets contained herein highlight 1999 EMSP-funded research projects; the original release date appears in the header of each individual Fact Sheet.

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EMSP
Environmental Management Science Program
Project Summary Fact Sheet • 1999 Awards

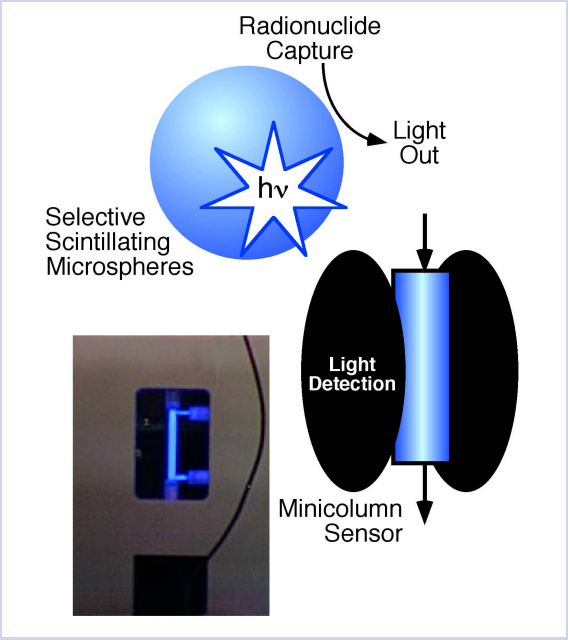
ANALYTICAL CHEMISTRY AND ACTINIDE CHEMISTRY

Leading academic and national laboratory scientists in these disciplines are participants in EMSP projects

Three 1999 EMSP projects have involved development of new analytical techniques for identification of contaminants in the field. Two other projects have focused on the chemistry of actinides in the environment.

Some of the leading groups researching analytical chemistry and instrumentation are involved in the three EMSP projects in this area. A novel system for detection of alpha- and beta-emitting radionuclides has received widespread notice in the analytical chemistry community, and continued development of the method is underway in one project. A second project involves a combination of selective surface coatings, electrochemistry, and spectroscopic detection to make a new, fieldable sensor for pertechnetate ions. A third project involves a diverse group of researchers from both universities and national laboratories who are working to develop a highly sensitive spectroscopic technique, i.e., resonant enhanced multiphoton ionization, into a field-deployable instrument for detection of organic compounds not easily determined by other means. If such a highly sensitive detector could be deployed with a cone penetrometer, the speed and accuracy for dense nonaqueous phase liquid (DNAPL) determinations could be improved by orders of magnitude over currently available techniques.

Both actinide chemistry projects are working to develop a more thorough understanding of the factors that could affect plutonium transport in the subsurface. One study has involved experimental determinations of plutonium species in the groundwater at Hanford and Savannah River and will illuminate the role that colloids play in plutonium transport. Another effort is directed toward understanding the role of manganese minerals in sequestering transuranics.



Selective Scintillating Microspheres for Analysis of Radionuclides

A Pacific Northwest National Laboratory/Clemson University group (70179) has developed a novel system for detecting radionuclides such as strontium-90, technetium-99, and actinides. The system is based on development of selective scintillating microspheres (SSMs).

Problems/Solutions

- As described in STCG Needs Statement OH-F004, laboratory analysis for technetium-99 in soil presently takes three days, and a need exists for an analyzer that can measure ^{99}Tc in the field and give results in a few hours. Two EMSP projects are directed toward solving this need, and one system has already been shown to detect ^{99}Tc in water at levels below the drinking water limits.
- Plutonium and actinides in groundwater can have widely varying transport properties that are dependent on distribution into colloid, particulate, and solution phases. One EMSP actinide chemistry project is providing detailed characterizations of the forms of plutonium present in Savannah River Site and Hanford groundwater so that more reliable predictions can be made about future migration patterns.

Anticipated Impact

- The need for long-term monitoring at U.S. Department of Energy (DOE) waste sites was described in *Long-Term Institutional Management of U.S. Department of Energy Legacy Waste Sites* (National Academy of Science, 2000) where it was noted that relatively few sites will be cleaned up to the point where they can be released for unrestricted use. Conventional sampling followed by laboratory analyses could present very large cumulative expenses, so new techniques of the type being developed in several EMSP projects could have very large impacts on expenditures for long-term monitoring.
- There are known to be more than 5,000 DOE groundwater plumes, which have in total contaminated more than 600 billion gallons of water and 50 million cubic meters of soil. Because many of these sites will require long-term monitoring by sensitive analytical techniques, continued improvements in sensitivity and portability of monitoring instruments can result in large savings over the monitoring lifetime.

Technical Summary and Progress

Analytical Chemistry

A New Sensor for Pertechnetate Ions. A University of Cincinnati/PNNL group (70010) is developing a sensor for technetium based on the general concepts that they used in a previous project (54674). To be detected, a species must first be incorporated into a film that is coated onto an optically transparent electrode. Then it must be reduced under the conditions used for an electrochemical process. Finally, the species formed by the electrochemical reduction must form a complex that absorbs light at the wavelength used for the optical detection. The research effort for this project is directed at developing the surface coatings, electrochemical conditions, and complexing agents that will enable a sensitive detection of pertechnetate. The goal is to be able to detect pertechnetate ions in the vadose zone without the elaborate sampling and separation procedures used for conventional analyses.

Selective Scintillating Microspheres for Analysis of Radionuclides. A PNNL/Clemson University group (70179) has developed a novel system for detecting radionuclides such as strontium-90, technetium-99, and actinides. The system is based on development of selective scintillating microspheres (SSMs). Thus, a minicolumn containing the bead materials is used to selectively bind the analyte. The SSMs, however, also contain scintillating materials that emit light when an alpha- or beta-emitting substance is on a nearby location in the bead, and a photomultiplier or diode sensor can then be used to detect the emitted light. A system designed for detecting technetium-99 was described in a paper in *Analytical Chemistry* that shows that the detection limit was 10 picograms per milliliter (below the maximum permissible drinking water level). Development continues on systems for selective detection of strontium-90 and actinides.

A Fieldable, Sensitive Technique for Detection of Organic Compounds. High-intensity visible light can be used to drive a molecular system through intermediate electronic states to a final state in which the molecule is ionized. Because ions can be detected with very high efficiency, this resonant enhanced multiphoton ionization (REMPI) process provides a sensitive analytical method. The goal of a University of South Carolina/LLNL project (70050) is to develop the REMPI technique using visible lasers for determination of compounds not easily detected by other methods. An objective is to develop a system for measuring and identifying volatile organic compounds (such as carbon tetrachloride, trichloroethylene, toluene, etc.) at parts-per-billion (ppb) levels *in situ* in the subsurface using a fiber-optic REMPI probe in a cone penetrometer. They have already demonstrated measurements of toluene at 1.5 ppb with a linear calibration curve for concentrations over a three-orders-of-magnitude range.

Actinide Chemistry

Speciation and Mobility of Actinides in Groundwater. The objective of a Woods Hole Oceanographic Institute/PNNL project (70132) is to gather fundamental data essential for predicting the migration of plutonium in an aqueous environment. In a previous project (54683), they developed special procedures for groundwater sampling that made it possible to separate plutonium into particulate, colloids, and dissolved phases. They determined isotopic ratios using the high sensitivity of thermal ionization mass spectrometry and showed that Pu in Savannah River Site (SRS) groundwater originates from both weapons-grade Pu and from a more mobile curium precursor. Most of the Pu at SRS is in an oxidized form that is more mobile than most standard models predict. Current work involves extensive sampling at the Hanford site in order to assist in the prediction of the migration potential. The main focus remains on identifying the Pu species present at Hanford, the mobility of these species, and the role that colloidal materials play in Pu transport.

Reactions of Transuranics on Manganese Oxide/Hydroxide Minerals. Manganese oxides, which are minor phases in the vadose zone, may preferentially sequester transuranics over iron oxide minerals. Thus, the objective of a LBNL/PNNL project (70176) is to provide information about the interactions of plutonium and neptunium with manganese-containing minerals. Sorption experiments performed with dilute solutions of Pu(VI and V) on various manganese minerals found that these minerals have a very large sorption capacity for plutonium under neutral or slightly basic conditions. The thermodynamic and kinetic parameters for the sorption on various manganese minerals will be used as input for reactive transport modeling of transuranics in the vadose zone.

Project Teams

Lead Principal Investigator (Award Number)

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  Pacific Northwest National Laboratory
- University of South Carolina
  PI: S. Michael Angel (70050)
  Lawrence Livermore National Laboratory
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  Pacific Northwest National Laboratory
- Lawrence Berkeley National Laboratory
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  Pacific Northwest National Laboratory
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ENGINEERING SCIENCE AND PLANT SCIENCE

Basic research in environmental engineering and plant science can contribute to practical remediation techniques/procedures

This fact sheet summarizes three 1999 EMSP projects that involve engineering science and one project classified as plant science. One of the environmental engineering projects involves a study of a process for the immobilization of chromium and other metals. The process involves the injection of gaseous hydrogen sulfide into the subsurface where it can reduce the soluble and mobile form of chromium, Cr(VI), into an insoluble and therefore less hazardous form, Cr(III). Details of this reaction in the presence of all the complexities presented by subsurface minerals are being studied in this project.

Two other engineering science projects are related to remediation of dense nonaqueous phase liquids (DNAPLs) in the subsurface. Surface vapor extraction has been used at several sites for removal of DNAPLs, and one project aims to understand factors that limit DNAPL removal rates with the goal of improving the efficiency of this technique. The second project is exploring the role that biologically produced surfactants may have in DNAPL mobility. Although this issue has been raised before, the subject has not been well studied. Identification and characterization of the role of these surfactants may be needed to develop more reliable DNAPL fate and transport models.

The plant science project is a continuation of a previous project in which it was demonstrated that native trees, shrubs, and grasses could be bioengineered to convert mercury into less hazardous forms. These plants thrive under conditions that would kill normal plants and may provide a more efficient, less costly method for removing mercury from surface soils.

Role of Surface-Active Materials on DNAPL Migration
A Clarkson University/Westinghouse Savannah River Company project (70035) sampled DNAPL– contaminated soil to better understand interrelationships affecting accumulation of DNAPL as a function of grain size, moisture content, and microbial activity in the vadose zone.

Problems/Solutions

- An STCG Needs Statement (RL-SS25-S) notes that "additional information is…needed about the role of surfactants and other agents on the basic physical properties (solubility, interfacial tensions) of NAPLs or dissolved organics and how these relations can be exploited to mobilize such contaminants." The goal of one EMSP project is to provide this information using both laboratory studies and field studies using core samples from a DNAPL plume at Savannah River Site.
- The removal of low, but hazardous, levels of mercury and other heavy metals from soils by traditional physical and chemical procedures can be very expensive. An EMSP project has worked on incorporating bacterial genes into native plants and trees so that they can accumulate mercury. These plants are able to thrive on levels of mercury that would kill normal plants, and they may provide an inexpensive means to concentrate mercury from surface soils.

Anticipated Impact

- A report of the National Research Council, *Research Needs in Subsurface Science* (March 2000), had on its cover an image of the mercury contamination in soil at the Y-12 plant at Oak Ridge, illustrating the importance of this problem. That report also cited the need for basic research focused on reactions for immobilization of hazardous metals in the subsurface. Both of these issues are being addressed by EMSP projects.
- In *Accelerated Cleanup – Paths to Closure*, nine of the ten U.S. Department of Energy (DOE) Operations Offices cited DNAPL contamination as a major concern. More reliable predictions of DNAPL migration are essential for decision-making regarding remediation expenditures, and existing remediation strategies need to be improved. Both of these needs are addressed by EMSP projects.

Technical Summary and Progress

Engineering Science

Immobilization of Metals by Reactions with Hydrogen Sulfide. Many metal ions form insoluble sulfides when exposed to hydrogen sulfide, H_2S, and the injection of gaseous H_2S into the subsurface has previously been suggested for immobilization of various hazardous metal ions. Chromium(VI) can also be reduced with H_2S to form chromium(III), which is not mobile, and a New Mexico Institute of Mining and Technology/PNNL project (70088) is focused on this process as a potential remediation technology. Some issues being addressed in laboratory studies include the effect of mineral surfaces on the rate of reduction of Cr(VI) as well as on the oxidation of H_2S by air, reactions of other soil minerals that could consume the H_2S, the long-term stability of Cr(III) species that are formed, and the effects of various soil water chemical compositions on the reduction reactions. Tests are also being conducted with Hanford soil samples to define reaction parameters for the Cr(VI)-H_2S-oxygen-soil system, and long-term oxidation tests will be conducted to ascertain the stability of the reduced chromium.

Project Teams

Lead Principal Investigator (Award Number)

- Clarkson University
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  Westinghouse Savannah River Company
- University of Illinois–Urbana-Champaign
  PI: Albert Valocchi (70045)
- University of Georgia
  PI: Richard B. Meagher (70054)
- New Mexico Institute of Mining & Technology
  PI: Baolin Deng (70088)
  Pacific Northwest National Laboratory

Factors that Limit the Effectiveness of Soil Vapor Extraction. Soil vapor extraction (SVE) is commonly used to remove DNAPLs from the vadose zone, but frequently a period of high recovery has been followed by a long period of low recovery. The research in a University of Illinois project (70045) aims to determine the processes that limit the removal of DNAPLs in heterogeneous porous media during SVE. Using magnetic resonance imaging, they can identify the location and size of individual pores containing DNAPLs, water, and vapor in flow-through columns filled with either model or natural sediments. Imaging results will be used along with modeling techniques to describe the transient distribution of phases as a function of time and location. These relationships will be used in a transport model to evaluate how different processes affect SVE performance in practical applications.

Role of Surface-Active Materials on DNAPL Migration. As anyone who has used a detergent knows, a small amount of a surfactant can have large effects on the interactions between dissimilar substances, i.e., oil and water. It would thus be reasonable to expect that surface-active chemicals present in the vadose zone could have a considerable effect on the migration of water-insoluble organic compounds, such as those classified as DNAPLs. Surface-active materials can be produced through microbial metabolic processes, and the goal of a Clarkson University/WSRC project (70035) is to understand the effects of various interfacial phenomena on the accessibility and migration of DNAPLs in the vadose zone. One objective is to identify the presence of surface-active materials and to quantify interfacial properties in an actual DNAPL plume at Savannah River Site. Other objectives include identifying how DNAPL–metabolizing cultures affect interfacial properties and quantifying the effects of DNAPL surface chemistry on flow in the vadose zone.

Plant Science

Phytoremediation of Mercury Pollution. A University of Georgia project (70054) is continuing work from a previous project (54837) to demonstrate that native trees, shrubs, and grasses can be engineered for remediation of mercury-contaminated sites. This group has engineered several plants to express two bacterial genes, *merB* and *merA*. Plants expressing *merA* extract and reduce ionic mercury to metallic mercury, which is transpired from the leaves. Those expressing *merB* extract highly-toxic methylmercury from the soil and degrade it to ionic mercury, and these plants are able to grow on concentrations of methylmercury that would kill normal plants. Plants expressing both *merA* and *merB* extract methylmercury and transpire metallic mercury. Current work is focused on obtaining a detailed understanding of the mechanisms by which these plants process the various forms of mercury in order to improve phytoremediation designs. In addition, attempts will be made to produce plants to accumulate mercury so that it can be removed by harvesting the plants rather than by vaporizing it into the environment.

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GEOCHEMISTRY AND BIOGEOCHEMISTRY

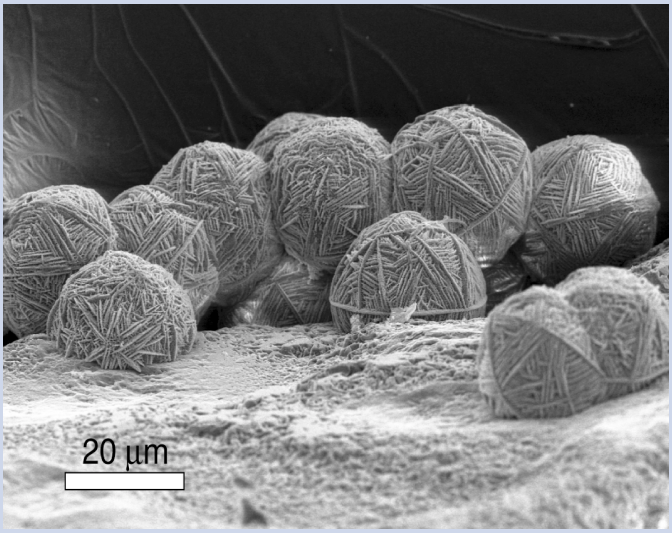
A THOROUGH UNDERSTANDING OF THE INTERACTION OF CONTAMINANTS WITH MINERALS IS ESSENTIAL FOR FATE AND TRANSPORT MODELING

Modeling of the fate and transport of radionuclides in the subsurface requires an understanding of the complex interactions among the numerous forms of radionuclides with the complex components of the vadose zone. Many 1999 EMSP projects are exploring issues related to contaminant transport. The subject of one study is how the migration of materials that leak from high-level storage tanks may be altered by changes caused by previous leaks, while the effects of subsurface reactions with highly alkaline solutions on immobilization of radionuclides is the focus of another project. Detailed characterizations of the interactions of radionuclides with calcium carbonate and with altered clay surfaces are the focus of several studies. Another is working on the thermodynamics of complexes formed by radionuclides in highly basic solutions. Technetium is of particular concern because it is easily oxidized to the highly soluble and mobile pertechnetate form, and another study is investigating reactions in the vadose zone that may reduce the pertechnetate to less mobile forms.

When precipitates are formed from solutions, they often trap other ions that would otherwise remain in solution. This method for removing radionuclides from solution has been employed since the earliest days of radiochemistry, and an EMSP project is investigating a process to form calcium carbonate precipitates in aquifers for *in situ* remediation of strontium-90 and other radionuclides.

One group is working on understanding the biological mechanisms involved in the reactions of a microorganism that can convert high concentrations of chlorinated hydrocarbons in the subsurface into less hazardous materials. The focus of another project is to develop an understanding of the vadose zone characteristics that encourage the growth of the same strain of bacteria.

Influence of Previous Tank Leaks on Migration of Subsequent Leaks



A University of Colorado/PNNL project (70070) is focused on obtaining a mechanistic understanding of how fluids that have leaked from Hanford single-shell tanks migrate through the vadose zone. Left: Nitrate cancrinite crystals formed on dissolving quartz grains after 13 days at 89°C from simulated waste tank solutions with pH 11.3, 2.1 molal sodium nitrate, and 0.01 molal aluminum. The ball-like precipitates cemented quartz grains together. Nitrate cancrinite is a zeolite-like phase that can incorporate cations such as cesium or strontium in its structure.

Problems/Solutions

- According to an STCG Need Statement (RL-WT053-S), "The current understanding of the mobility of contaminants from single-shell tank leaks…is inadequate to fully support cleanup, closure, or performance assessment-related decisions. Without knowledge about the distribution of contaminants beneath the tank farms, and without the ability to predict contaminant movement, it will be impossible to assure the public that the U.S. Department of Energy (DOE) can predict the impact of leaks during sluicing and the impact of leaving the tanks in place." Seven projects are addressing issues directly related to this need.
- As stated in an STCG Need (ID-S.1.10), "Geochemistry of Contaminants in the Vadose Zone," no correlation between substrate properties, solution chemistry, and the measured adsorption constant values has been determined for the vadose zone at most sites. Thus, the smallest available adsorption constants for binding radionuclides to minerals are used in predictive models to compensate for the lack of theoretical understanding. This may result in undertaking unnecessary remedial actions. Several EMSP studies are measuring binding constants of radionuclides to a variety of minerals relevant to this issue.

Anticipated Impact

- Effective biodegradation of chlorinated hydrocarbons has advantages over physical removal methods in cost, speed, public acceptance, and final cleanup levels achieved. Several projects are focused on explorations of conditions that favor the use of biodegradation techniques.
- Sixty-seven of the single-shell tanks at Hanford are thought to have leaked a total of up to a million gallons of highly alkaline fluids containing substantial quantities of radionuclides into the subsurface. Most of the 1999 EMSP projects are exploring issues related to the migration of contaminants in the subsurface so that future remedial actions can be based on sound scientific knowledge.

Technical Summary and Progress

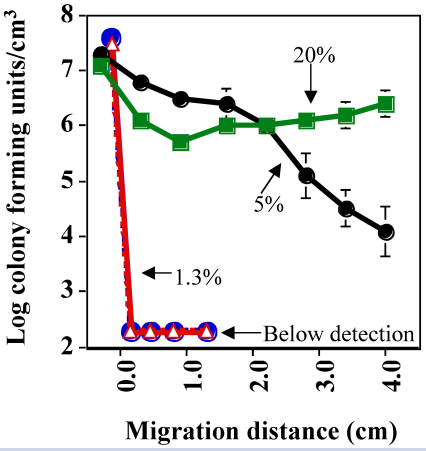
Characterization and Modeling of the Properties of the Vadose Zone

Influence of Previous Leaks from Tanks on Migration of Subsequent Leaks. Transport of the high ionic strength, high pH solutions through the vadose zone is dependent not only on the initial subsurface characteristics but also on chemical reactions from previous leaks that may have altered the properties of the subsurface. A University of Colorado/PNNL project (70070) is focused on obtaining a mechanistic understanding of how fluids that have leaked from the Hanford single-shell tanks migrate through the vadose zone. The first goal is to obtain kinetic rate laws for the dissolution of quartz and feldspar, as well as the precipitation of secondary phases, when tank liquids contact them. They will attempt to obtain an understanding of the nucleation mechanisms, nucleation sites on soil minerals, and the role of reactive surfaces on dissolution and precipitation reactions.

Transport of Radionuclides in Subsurface Solids Impacted by Alkaline Tank Fluids. An Ohio State University/PNNL/Stanford University project (70081) is directed toward understanding how the most common radionuclides might become immobilized in the subsurface solids that have been impacted by alkaline tank fluids. The effect of aging on the stability of complexes on solids formed from neutralization and nucleation of alkaline aluminate solutions is being investigated, and the sorption or co-precipitation of various radionuclides in the solids formed by reactions of alkaline aluminate solutions with various minerals and with Hanford sediments is being studied. They also plan to use a variety of modern instrumental methods to characterize the chemical forms of the species present in actual core samples taken from underneath the SX-108 tank.

Sorption of Cesium and Strontium on Altered Clay Surfaces. The focus of a Pennsylvania State University/BNL/PNNL (70126) project is on the extent of sorption and release of cesium and strontium on purified clays (illite, vermiculite, montmorillonite, and kaolinite) during the reaction with solutions similar to those encountered beneath leaking high-level storage tanks. Sorption studies on clays have shown that the extent of Sr sorption is higher than for Cs, except in the case of illite. Kinetic studies show that Cs/Sr uptake on clays is strongly controlled by secondary mineral formation, with the types of phases formed being dependent on each clay system and initial contaminant concentrations. Nuclear magnetic resonance, X-ray diffraction, and X-ray absorption spectroscopy techniques are being used to characterize the coordination environment of the sorbed ions. Their results are intended to be applied in equilibrium and transport models for radionuclide distribution between solid, colloidal, and dissolved phases.

Role of Calcium Carbonate Grain Coatings on Contaminant Migration. Calcium carbonate exists as grain coatings and intergrain fill in the vadose zone at Hanford. The goal of a PNNL/Stanford University/University of Wyoming project (70121) is to understand the interaction of some contaminants (strontium-90, cobalt-60, chromate, and pertechnetate) with these materials in order to improve forecasts of contaminant migration. Questions being addressed include: (1) Do carbonate coatings form preferentially on particular mineral surfaces? (2) Do carbonate coatings inhibit electron transfer reactions at otherwise reactive surfaces? and (3) Do carbonate coatings enhance the binding of species such as ^{90}Sr and ^{60}Co?



Impact of Vadose Zone Properties on Microorganism Colonization A PNNL/Oregon State University project (70165) is focusing on the ability of strain KC to colonize sediment from a single inoculation point as a function of vadose zone characteristics. Above: Migration of bacteria after 120 hours in static (no flow) unsaturated columns containing 1.1 mm sand; bacteria were inoculated at 0.0 cm. Migration decreased with decreasing volumetric water contents (green, black, red) when nutrients were not supplied in the column. Water content of 1.3% prevented movement of bacteria even in the presence of nutrients (blue).

Characterization of Metal Ions Bound to Calcium Carbonate Surfaces. A State University of New York–Stony Brook/PNNL project (70146) is designed to assess the role of calcium carbonate in the uptake and retention of inorganic contaminants, such as cobalt, cesium, lead, strontium, and chromium. Their work has made extensive use of the National Synchrotron Light Source at Brookhaven and the Advanced Photon Source at Argonne for detailed microscopic and spectroscopic characterization of the interactions of various metal ions with carbonate surfaces. Early work showed that the detailed structure of the carbonate surface controls the extent to which chromate is removed from vadose-zone fluids, and similar work is exploring uranyl uptake on carbonate surfaces. They have also shown that only a small fraction of a natural caliche surface offers favorable reaction sites for lead uptake. X-ray absorption fine structure spectroscopy and X-ray fluorescence techniques are being used to characterize the binding of various metal ions to carbonate surfaces.

Thermodynamics Parameters for Radionuclide Species in Highly Basic Solutions. Highly basic solutions can dissolve large concentrations of silica from minerals present in the subsurface, and the resulting solutions can form stable complexes with radionuclides and hence enhance the transport of radionuclides. A PNNL/Florida State University project (70163) is working on the thermodynamics of the species formed by radionuclides in highly basic solutions, particularly those with high silica concentrations. Their work includes experimental determinations of the species present in solution, molecular simulations to help identify species structures, and physical chemistry measurements to obtain the thermodynamic data necessary for predicting contaminant complexation and waste neutralization reactions.

Mobility of Technetium in the Vadose Zone. A PNNL/LANL project (70177) is focused on reactions in the vadose zone that may decrease the mobility of the technetium that has been released at Hanford. Technetium is easily oxidized to form the highly soluble and mobile pertechnetate species, but reduction reactions on iron(II)-containing mineral surfaces could result in forming technetium dioxide and other reduced species with much lower mobility. Their first goal is to develop a description of the reduction of pertechnetate ions on iron(II)-containing minerals, and they have characterized the amorphous technetium dioxide formed by both hydrazine and reduction with an iron-reducing bacterium. They plan to determine the stability of the reduced technetium solids and to use contaminated Hanford sediments to validate their models of technetium mobility in the vadose zone.

Chemical Treatment of the Saturated Zone

In Situ Formation of Calcium Carbonate to Immobilize Radionuclides. An INEEL/Portland State University/University of Toronto project (70206) is directed toward a remediation technique that uses the formation of calcium carbonate precipitates to trap radionuclide contaminants. The idea is to inject urea into a contaminated aquifer. If urease-containing organisms are present, the urea will be hydrolyzed to form ammonium carbonate, which will react with low concentrations of calcium to form calcium carbonate and trap other metal ions in the precipitate. Early results indicated that the potential for using urea hydrolysis as the basis for an *in situ* remediation technique for strontium-90 and other divalent metal ions is promising. Urea-hydrolyzing bacteria were found in the Snake River Plain Aquifer at INEEL, and it was found that these bacteria can catalyze formation of calcite in the presence of urea.

Project Teams

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  Oregon State University
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  PI: Nancy J. Hess (70177)
  Los Alamos National Laboratory
- Idaho National Engineering & Environmental Laboratory
  PI: Robert W. Smith (70206)
  Portland State University
  University of Toronto

Bioremediation in the Subsurface

Biodegradation of DNAPLs. Biodegradation of concentrated chlorinated solvents was previously thought not to be possible because these solvents are toxic to microorganisms, but a Stanford University project (70063–a renewal of 54666) is exploring use of anaerobic biodegradation in regions near DNAPL plumes. They demonstrated the potential of certain microorganisms to reductively dehalogenate tetrachloroethylene and other chlorinated ethenes at high concentrations, and their work demonstrated the advantage that can be achieved by carrying out *in situ* dehalogenation directly on DNAPL rather than on more dilute solutions. The group is attempting to provide a molecular understanding of the biological mechanisms involved in the reactions and to determine the cellular components involved in carbon tetrachloride transformation by a *Pseudomonas stutzeri* strain KC without the formation of chloroform.

Impact of Vadose Zone Properties on Microorganism Colonization. Injection of non-engineered microorganisms and aqueous-based nutrient delivery are potentially acceptable technologies at DOE sites, and a PNNL/Oregon State University project (70165) is also exploring use of the same *Pseudomonas* strain for DNAPL remediation. However, the focus of their work is on the ability of strain KC to colonize sediment from a single inoculation point as a function of vadose zone characteristics, such as water-filled porosity, pore throat size, aqueous nutrient concentration, and distance from a nutrient injection point. Researchers in this project are also modifying a widely used computer program for vadose zone flow and transport modeling to include coupled biological and hydrologic processes.

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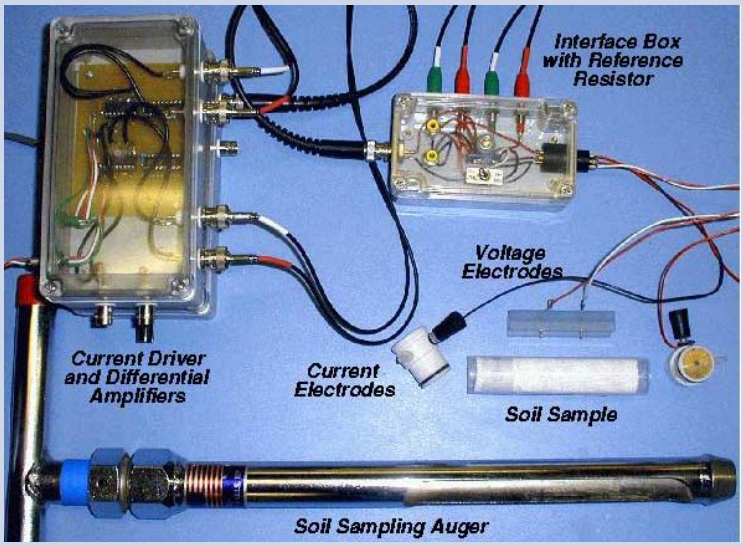
GEOPHYSICS

Geophysical methods are essential for large-scale characterization of subsurface properties

Dense nonaqueous phase liquids (DNAPLs), mostly chlorinated hydrocarbons, were widely used in the U.S. Department of Energy (DOE) complex, and thousands of gallons were released into the subsurface. Thus, a high-priority need at many sites is a reliable method to locate DNAPLs in the subsurface without direct sampling via boreholes. One 1999 EMSP project is developing use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface, while another project is focused on use of ground-penetrating radar for direct detection of DNAPLs.

Predictions of contaminant transport in the subsurface require an understanding of the properties of the region between the surface and the groundwater, i.e., the vadose zone. Major efforts by many subsurface scientists are directed toward use of geophysical tools for more precise determinations of subsurface properties. EMSP projects in this area include an effort to develop relationships between measured geophysical properties and porosity, saturation, and fluid distributions in the vadose zone. Another study is focused on expanding the usefulness of ground-penetrating radar methods for the determination of moisture content in the vadose zone, while another project is designed to improve the usefulness of high-frequency electrical impedance methods for determinations of the amount and composition of fluid present in porous media. A diverse group of researchers is working on a project to develop a hydrologic-geophysical method for characterizing flow and transport in the vadose zone. Their work involves electrical resistance tomography, ground-penetrating radar measurements, and new computational codes to analyze flow during a hydrologic field experiment. The hybrid hydrologic-geophysical inverse technique uses work done in a previous EMSP project.



Complex Electrical Resistivity Measurements
A New England Research project (70012) is working on use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface. Above: Principal components for laboratory measurement of frequency-dependent electrical resistivity of soils. Samples obtained in the field with the hand auger can be studied immediately with minimal disturbance to the soil structure.

Problems/Solutions

- As noted in *Research Needs in Subsurface Science* (National Research Council, 2000), "currently available indirect methods…are inadequate for locating most types of contaminants in the subsurface, and direct methods such as drilling are both expensive and limited in effectiveness." The report suggested that there is a high-priority need for research on improved indirect methods for measuring contaminant and subsurface properties, and EMSP projects are focused on this goal.
- Similar needs have been cited in many STCG Needs Statements. For example, RL-SS31 notes that only a low percentage of subsurface contaminants has been located in the vadose zone and that "characterization methods are needed to define the *in situ* physical and chemical aspects of the vadose zone, and average field-scale properties describing fluid flow and reaction. These methods need to have the sensitivity to characterize subsurface geohydrologic and geochemical properties with sufficient accuracy to permit prediction of contaminant fate and transport." Many EMSP projects are not only working on innovative characterization tools, they are also testing them in the field at contaminated DOE sites.

Anticipated Impact

- DOE waste sites are found over a wide range of hydrogeologic settings, so the containment, removal, or treatment of subsurface contaminants at one site may involve quite different challenges than those encountered at other sites. Contamination occurs in thick unsaturated zones, in high- and low-permeability soils, in aquifers, and in fractured basalt and karst bedrock. Therefore, many different geophysical techniques are being explored by EMSP projects in order to maximize the widespread applicability of the results to problems faced by the full range of DOE sites.

Technical Summary and Progress

Monitoring DNAPLs in the Subsurface

Complex Electrical Resistivity Measurements. Researchers in a New England Research project (70012) are working on use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface. The work is based on a four-electrode electrical resistivity measurement, where two electrodes are used to impose a sinusoidal current and the remaining two sense the response voltage of the sample. The phase lag between the source and response signals at low frequencies is the measured parameter thought to be characteristic of certain organic solvents in clay-bearing soils. Early work involved developing a system to resolve complex resistivity phase angles of a milliradian over a wide frequency range.

Ground-Penetrating Radar. A University of Wyoming project (70052) is directed toward use of ground-penetrating radar for direct detection of DNAPLs. Most organic liquids have lower dielectric permittivity and conductivity than does water, so a contrast in properties is induced when DNAPLs displace water. This project focuses on three aspects of reflected wave behavior: propagation velocity, frequency dependent attenuation, and amplitude variation with offset. The objectives are to develop a suite of methodologies for direct detection of DNAPLs, to perform field verifications at well-characterized, contaminated sites, and to do contaminant detection in a field setting with subsequent verification through direct sampling.

Project Teams

Lead Principal Investigator (Award Number)

- New England Research, Inc.
  PI: Stephen R. Brown (70012)
- University of Wyoming
  PI: John Bradford (70052)
- Lawrence Livermore National Laboratory
  PI: Patricia A. Berge (70108)
- Stanford University
  PI: Rosemary Knight (70115)
  University of British Columbia
- Sandia National Laboratories–Albuquerque
  PI: Gregory A. Newman (70220)
  ElectroMagnetic Instruments, Inc.
- University of Wisconsin–Madison
  PI: David L. Alumbaugh (70267)
  Sandia National Laboratories–Albuquerque

Characterization of Properties of the Vadose Zone

Improved Geophysical Imaging Techniques. An LLNL project (70108) is developing relationships between measured geophysical properties and porosity, saturation, and fluid distribution for partially saturated soils, such as those found in the vadose zone. This work is a continuation of a previous project (55411) aimed at improving geophysical imaging techniques. An ultrasonic apparatus for simultaneously measuring compressional and shear wave velocities was modified to enable measurements on partially saturated soil samples. Other work has involved X-ray computed tomography imaging of moisture distribution in sands, using the Advanced Photon Source at Argonne. Future work will focus on developing algorithms for relationships between composition, saturation, and geophysical measurements.

Determination of Moisture Content in the Subsurface. The objective of a Stanford University/University of British Columbia project (70115) is to develop the usefulness of radar methods for the determination of moisture content because contaminant transport in the vadose zone is very dependent on moisture content. Their work is focused on (a) the relationship between the dielectric constant of a subsurface volume and the moisture content of that volume and (b) the use of radar data to obtain information about the spatial variation of moisture content. They plan to develop a model for the joint inversion of geophysical and hydrological data to obtain hydrological parameters.

High Frequency Impedance Methods. Electromagnetic methods are sensitive to the amount and composition of fluid present in porous media. High-frequency impedance methods are particularly useful for situations in which ground-penetrating radar cannot explore sufficient depths. A SNL/ElectroMagnetic Instruments project (70220) is designed to improve the usefulness of this method. Their work involves the development of nonlinear 2D/3D inversion solutions and the use of these solutions to improve image resolution. The goal is to collect impedance measurements at the Hanford site and to interpret the field data with the newly developed inversion techniques along with independent information from other sources.

A Hydrologic-Geophysical Method. A University of Wisconsin/SNL project (70267) is working on a hydrologic-geophysical method for characterizing flow and transport processes within the vadose zone. The method uses electrical conductivity information from electric resistivity tomography, dielectric constants obtained from cross-borehole ground-penetrating radar, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data to provide maps of hydrogeological heterogeneity and extent of contamination. This work uses some methods developed by another project (55332). The geophysical imaging techniques will be used to image the changes produced by transport experiments as they occur, and the data will provide checks for the numerical flow and transport simulations.

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HYDROGEOLOGY

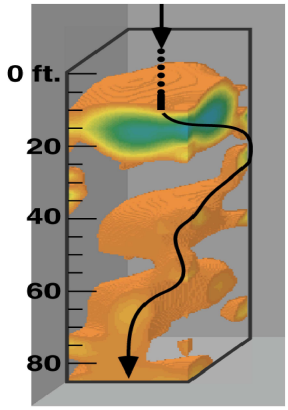
Understanding how water flows through diverse geologic structures is essential for understanding contaminant migration

Several 1999 EMSP projects are working on various aspects of flow and transport in the vadose zone, which is the region between the soil surface and the groundwater. The physics of fast flow processes in coarse-textured media is fundamentally different from that of flow in finer-textured media, and one project is attempting to improve understanding of this phenomenon because it may be important at several U.S. Department of Energy (DOE) sites. Another project is conducting both experimental and modeling studies of subsurface structures that may allow preferential vertical flow paths, because even small concentrations of such structures could have a profound influence on the total downward migration of contaminants.

The "Vadose Zone Observatory" at Lawrence Livermore is a facility with numerous geophysical and hydraulic observational instruments throughout the 70-foot vadose zone. This facility is being used by one research group to show how vadose zone characteristics influence the transport of contaminants down to the water table. Another diverse group of researchers is using small-scale direct measurements of soil properties along with geophysical techniques to develop large-scale predictions of transport properties. The fate and transport of radionuclides beneath the Hanford tank farm are the subject of a project in which the researchers have obtained both horizontal and vertical undisturbed core samples to enable realistic laboratory studies of the transport properties of materials similar to those beneath the tanks.

In recent years it has become clear that some radionuclides can become suspended in colloids that will result in much greater mobility than anticipated on the basis of the solubility of the radionuclide species. One project is investigating such colloid-facilitated transport.

Vadose Zone Observatory Salt Water Infiltration



Saturation changes at bottom of VZ in less than 6 hours

Vadose Zone Observatory

An LLNL project (70149) is using infiltration experiments at a Vadose Zone Observatory to show how vadose zone characteristics influence transport of contaminants to the water table. Left: An ERT image showing the electrical conductivity distribution less than 6 hours after a 1,500-liter infiltration event using very saline water. The water table is normally below 65-70 feet, but the salt water signal appears to have actually penetrated below the water table owing to its greater density. This result, in conjunction with a related tracer study, strongly suggests that fast paths can carry at least part of the "contaminated" water rapidly to the water table.

Problems/Solutions

- As described in an STCG Science Need Statement (RL-SS29-S), "The science needed to elucidate the role of physical and chemical heterogeneities on subsurface transport of solutes and colloids can be focused on both (1) developing a more thorough understanding of the relative contributions of these heterogeneities to contaminant transport through controlled experimentation, and (2) rapidly and accurately characterizing the presence of these heterogeneities." These are precisely the subjects being addressed by EMSP projects in this area.
- As noted in an STCG Science Needs Statement (RL-SS29-S), "knowledge of how heterogeneous physical and chemical properties affect chemical solute and colloidal transport is important to the design of appropriate remedial technologies. Key science issues related to how physical properties affect transport include determining the effect of multidomain pore structures on contaminant transport rates, determining the role of pore structure on the movement of water in unsaturated porous media, and relating this information to convective and diffusive transport of contaminants." These are some of the areas being pursued by researchers on EMSP hydrogeology projects.

Anticipated Impact

- Only a low percentage of the total radionuclide and hazardous materials in the subsurface at DOE sites has been thoroughly located and characterized. Even if the entire inventory of contaminants was located, most sites with low levels of contamination could not be treated to remove the contaminants because of the high cost-to-benefit ratios. Thus, it is especially important that reliable hydrogeology information is available to enable sound scientific predictions of the fate and transport of contaminants so that remediation resources can be used where the benefits will be the greatest.

Technical Summary and Progress

Hydraulic Properties of Coarse Sediments. An LBNL project (70069) is designed to improve understanding of flow in coarse-textured media such as those at Hanford. The objectives are to quantify the macroscopic hydraulic properties of very coarse sediments and to determine the microscale basis for fast unsaturated flow. Macroscopic studies have used several column methods. The microscopic tests of film flow have used the National Synchrotron Light Source at Brookhaven to determine average water film thicknesses on Hanford gravel samples. The combined results of macroscopic and microscopic experiments will be used to develop a physical model of unsaturated flow in coarse sediments.

Preferential Flow in Vertical Paths. Most flow and transport models of the vadose zone have assumed horizontally layered sediments with no preferential vertical flow paths. But preferential flow through vertically oriented, more highly permeable structures may enhance movement of moisture and contaminants through the vadose zone. A PNNL/New Mexico Institute project (70193) is exploring field and modeling studies of these clastic dikes. They have used a detailed ground-penetrating radar survey to identify dike spacing and thickness, and are measuring the distribution of hydraulic properties within dikes using infiltration experiments.

Project Teams

Lead Principal Investigator (Award Number)

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- Washington State University
  PI: Markus Flury (70135)
- Lawrence Livermore National Laboratory
  PI: Charles R. Carrigan (70149)
- Pacific Northwest National Laboratory
  PI: Philip D. Meyer (70187)
- Pacific Northwest National Laboratory
  PI: Christopher J. Murray (70193)
  New Mexico Institute of Mining & Technology
- Oak Ridge National Laboratory
  PI: Philip M. Jardine (70219)
  Pacific Northwest National Laboratory
  Stanford University

A Vadose Zone Observatory. An LLNL project (70149), which is a continuation of project 54950, is using infiltration experiments at a "Vadose Zone Observatory" to show how vadose zone characteristics influence the transport of contaminants to the water table. The LLNL facility contains wells with geophysical instruments, tensiometers, lysimeters, and other sensors throughout the vadose zone. One experiment involved infiltrating water and tracking the downward transport of tracers previously added to the soil. This mimics a cleaning of Hanford tanks when leakage of uncontaminated water might mobilize existing soil contamination. Electrical imaging tracks the development of a groundwater plume as the injected water moves to the water table.

Modeling Flow and Transport in the Heterogeneous Vadose Zone. A PNNL project (70187) is using small-scale direct measurements of soil physical and hydraulic properties (hard data) along with indirect geophysical measurements (soft data) to develop a systematic approach for parameterization of numerical models for simulation of field-scale flow and transport problems. Data from controlled field experiments at Hanford are being used to evaluate the parameterization methods. Neural network analyses are also being applied to develop pedo-transfer functions for relating soil texture and bulk density data to hydraulic properties. The prediction uncertainty associated with using sparse and/or surrogate data for model parameterization is being addressed.

Migration of Radionuclides beneath the Hanford Tanks. The fate and transport of radionuclides beneath the Hanford tank farms are the subject of an ORNL/PNNL/Stanford University project (70219). They obtained both horizontal and vertical undisturbed core samples from a Hanford location. The transport of several tracers will be investigated at a variety of water contents reflective of the range of recharge rates at Hanford. Preliminary results suggest that lateral flow beneath the tank farms is a strong contributor to the spread of contaminants. In addition to the macroscopic fate and transport experiments, interfacial molecular techniques will be used to quantify the distribution and chemical environments of the sorbed contaminant species. The goal is to provide an improved understanding and predictive capability for the fate of the radionuclides that have leaked from the Hanford tanks.

Colloid-Facilitated Transport of Radionuclides. A Washington State University project (70135) is designed to study colloid-facilitated transport of radionuclides. The first objective is to determine the characteristics of the colloidal particles that form under conditions similar to those found beneath the Hanford tanks. Next, the interactions between colloids, contaminants, and the soil matrix will be studied under various ionic strength and pH conditions, and the mobility of colloids through the soil will be evaluated. Preliminary experiments have shown that a considerable amount of colloidal particles can be mobilized when a concentrated salt solution infiltrates the Hanford sediments and is subsequently diluted.

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LOW-DOSE RADIATION

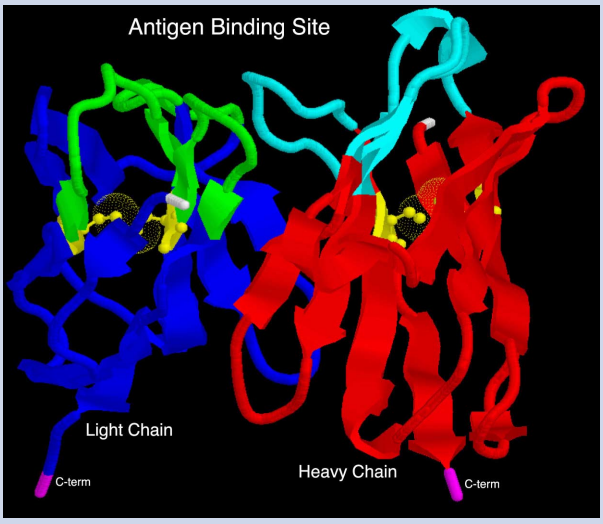
Is the biological damage induced by low doses of radiation repaired with the same efficiency as normal oxidative damage?

The Notice Inviting Grant Applications for the EMSP projects described here suggested that research was needed to understand the normal cellular processes responsible for repairing oxidative damage and radiation-induced damage. If it could be proved that there is no enhanced cancer risk with radiation exposures up to some threshold, the end point for remediation activities could be defined more precisely and wasteful remediation activities that would provide no benefit could be avoided.

Radiation damage in DNA is caused by free-radical reactions initiated by ionization events, and one EMSP project is attempting to determine if conventional laboratory results overestimate *in vivo* cellular responses because of higher oxygen concentrations. A unique focused X-ray facility is being used by another group to study the effects of low-dose radiation on single cells that absorb the radiation as well as on neighboring cells that are not directly exposed.

One EMSP project was designed to determine whether there is an adaptive response against neoplastic transformation by ionizing radiation, and another is investigating why low-dose exposures induce resistance to damage from subsequent exposures. Another effort is directed toward development of tools to allow more sensitive visualization of double-stranded DNA break repair complexes so that the formation of repair complexes can be studied at lower exposure levels. The detection of changes in certain molecular events in cells due to radiation exposures may provide a sensitive method for detecting effects of radiation exposure, and another project includes a determination of whether the use of such methods *in vitro* can be used to reliably predict *in vivo* processes.

Variations in DNA repair mechanisms could make some individuals more susceptible to radiation-induced cancers than normal, and an EMSP project is studying the effect of one hereditary disorder on risk due to low-level radiation. Finally, a social science project is directed toward understanding individual, group, and community responses to perceived radiation risks.



Better Determinations of Health Risks
A Medical College of Georgia project (69906) is developing tools to allow direct *in situ* visualization of double-strand DNA break repair complexes. The project uses genetically engineered single chain antibody and digital image processing technologies. Left: Recombinant single chain antibody directed against the DNA repair protein, DNA-PKcs. Ribbon diagram shows model of antibody heavy and light chain domains (red and blue), each stabilized by a disulfide bond (yellow), with antigen binding site marked.

Problems/Solutions

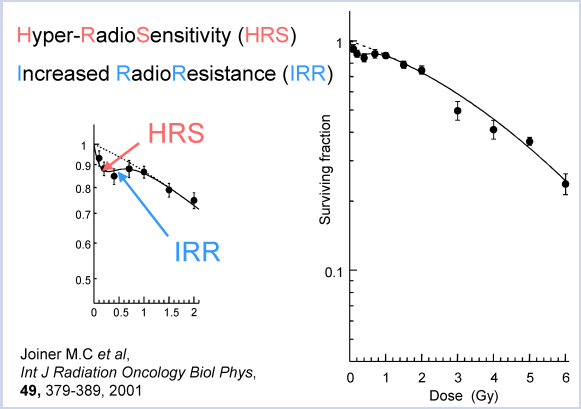
- More than 100,000 single-strand DNA breaks per day occur in each cell in our bodies due to normal processes, and the additional breaks due to low-level radiation are a tiny fraction of the total. Thus, the fundamental issue is whether the amount and kinds of DNA damage produced at low doses of radiation are different from those normally produced within cells. Several EMSP research efforts are contributing to a basic understanding of the molecular processes that follow the absorption of ionizing radiation.
- Despite the fact that the frequency of double strand breaks is much lower than that of other types of damage, double strand breaks may be the major determinant that distinguishes normal oxidative damage from low-dose radiation induced damage to DNA. The goal of an EMSP project is to develop tools to allow a two-orders-of-magnitude increase in sensitivity over existing methods for measuring double-strand breaks.

Anticipated Impact

- The goal of all remediation work with radioactive waste is to minimize impacts on the health of living species. If it can be proved that there are dose thresholds below which no biological responses or increases in radiation risk occur, then the endpoint of remediation can be clearly defined. If it is assumed that no radiation exposure is risk free, then it is difficult to define standards for free release of any site.
- All the information for radiation-induced DNA damage is from data obtained at high doses; there are no data at the low doses that could occur at formerly contaminated sites after remediation. It is essentially impossible to determine by direct observation in animals increased cancer risks due to acute exposures to 10 rem or 0.1 Sv, so several EMSP projects are working on development of techniques that may be able to detect changes in certain molecular events that are prerequisites to the development of observable cellular abnormalities.

Comparisons of the Effects of Low-Dose Radiation and Normal Oxidative Damage

Gamma radiation (for example) produces most of its effects through the generation of reactive oxygen species, which are also produced by normal metabolic processes. Most *in vitro* experiments are conducted in air where oxygen is present at six times its *in vivo* physiological concentration, so the unnaturally high levels of oxygen may distort the true cellular response to low-level ionizing radiation. A LANL project (69938) will compare the consequences of inducing genetic damage either by radiation or by temporary exposure to elevated oxygen concentrations. Their "oxidative stress laboratory" will also be used to investigate whether the reported beneficial effects of low-radiation doses result from triggering an antioxidant defense mechanism.

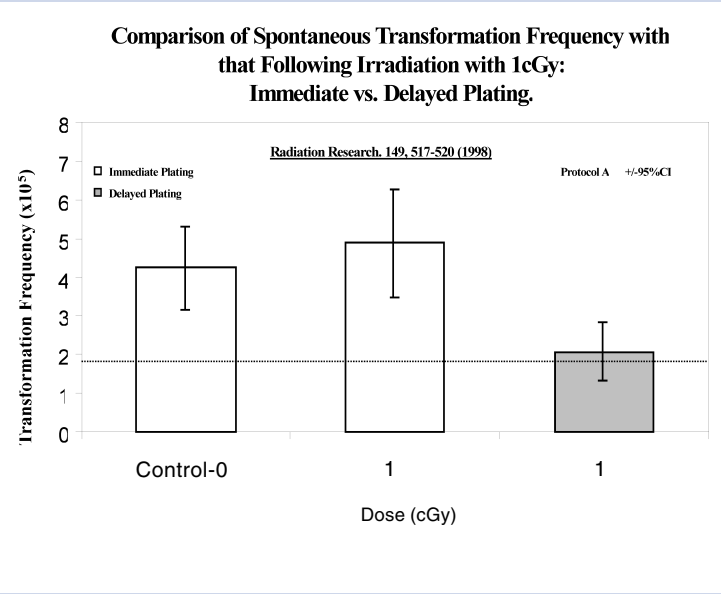


Low-dose hyper-radiosensitivity (HRS) and increased radioresistance (IRR)
The overall aim of a Gray Laboratory Cancer Research Trust project (69981) is to acquire an understanding of the mechanisms underlying low-dose HRS and IRR. Above: Sub-structure in the survival response of cells to low-LET ionizing radiation at less than 1 Gy, shows the HRS region of low-dose HRS below 20 cGy. Above 20 cGy, IRR occurs. Thus the low-dose response is considerably greater than predicted by the high-dose response, and has to be measured separately.

The objective of the Gray Cancer Research Trust (UK)/ Massachusetts General Hospital project (69980) is to increase understanding of the responses of cells to the low doses of ionizing radiation typically encountered in environmental exposures. The researchers use a unique focused X-ray facility for irradiation of individual cells or even subcellular regions. Prior single-cell irradiation studies with this facility gave evidence for bystander responses in unirradiated cells and a dose-effect relationship that indicated a low-dose threshold. The goals for this project include determinations of the responses of individual cells to low doses of X-rays as well as determinations of the response of cells to reactive oxygen species generated by chemical agents in a fashion similar to normal cellular processes. Other objectives include investigations of the interactions between oxidative processes and ionizing radiation and determinations of the effects that reactive species or radiation in an individual cell can cause in surrounding, untreated cells.

Better Determinations of Health Risks Due to Exposures to Low-Dose Radiation

How much do low doses of radiation protect against subsequent low doses of ionizing radiation? The experiments being undertaken by a University of California–Irvine project (69848) are designed to address this question. They will measure the neoplastic transformation frequency in a skin fibroblast human hybrid cell system as a function of exposures to gamma and X-rays. Total doses will be 0, 0.1, 1.0 and 10 centiGrays (1 rad) and will include single and multiple exposures to reach the total dose. These experiments are designed to provide information required to determine whether there is an adaptive response against neoplastic transformation by ionizing radiation. Earlier studies (*Radiation Research* 149: 517-520, 1998) demonstrated the induction of a significant adaptive response against spontaneous neoplastic transformation by a dose of 1 cGy of ^{137}Cs gamma radiation. Preliminary data from the current project indicate a similar adaptive response at single doses as low as 0.1 cGy and as high as 10.0 cGy.



Adaptive Response
A University of California–Irvine project (69848) is investigating to what degree low doses of radiation protect against subsequent low doses of ionizing radiation. Above: Adaptive response against spontaneous neoplastic transformation induced by 1 cGy of ^{137}Cs gamma radiation.

Without radiation exposure, single strand breaks in DNA occur at a rate of 150,000 per day per cell, and exposures at the upper limit of low-level radiation cause about 200 per cell. But perhaps the double-strand DNA breaks (DSBs) induced by radiation are more important, and a Medical College of Georgia project (69906) is directed toward developing tools to allow direct *in situ*

visualization of DSB repair complexes. This work may provide an improvement of two orders of magnitude in sensitivity over existing methods of measuring double-strand breaks. The project uses genetically engineered single chain antibody and digital image processing technologies. If the approach proves successful, it will be used to compare the formation of repair complexes at various dose levels and to study the effect of low doses on the response to subsequent higher doses.

The most conservative cancer risk assessments are based on linear extrapolations of high dose data to low doses, but the existence of repair mechanisms would suggest that linear extrapolations to low doses are not reasonable. A PNNL study (69941) is developing the molecular tools necessary to define thresholds in cell signaling pathways that are required for cellular transformation and that may be affected by low-dose radiation. They are investigating the effects of low-dose radiation exposures on certain molecular events in a well-characterized system of mouse cells, and they plan to determine whether the low-dose radiation responses demonstrated *in vitro* are relevant to *in vivo* processes using a standard mouse skin initiation-promotion strategy.

The overall aim of a Gray Laboratory Cancer Research Trust (UK) project (69981) is to acquire an understanding of the mechanisms underlying low-dose hyper-radiosensitivity (HRS) and increased radioresistance (IRR). They have shown that cell lethality measured after low-dose exposure to gamma- or X-rays is markedly enhanced relative to that expected by extrapolation of the high-dose response. This may compensate for processes that would lead to cancer formation at low doses and suggests that the adverse effects of small radiation doses could be overestimated. Specific goals of the project are to identify which aspects of DNA repair determine HRS and IRR, to investigate changes in DNA structure and conformation that may change the DNA repair rate, and to determine whether the adaptive response and HRS/IRR are separate or interlinked phenomena.

Project Teams

Lead Principal Investigator (Award Number)

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- Decision Science Research Institute
  PI: James Flynn (69904)
- Medical College of Georgia
  PI: William S. Dynan (69906)
- Los Alamos National Laboratory
  PI: Edwin H. Goodwin (69938)
- Pacific Northwest National Laboratory
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- Gray Laboratory Cancer Research Trust (UK)
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Genetic Factors that Affect Susceptibility to Low-Dose Radiation

Are there genetic differences that make some individuals more susceptible to radiation-induced cancers than normal? Variations in DNA repair mechanisms or conditions that provide a differential growth advantage for mutated cells could provide enhanced susceptibility. The goal of a PNNL project (69939) is to determine whether persons with hereditary hemochromatosis (HH) would have an increased susceptibility to cancer induced by low-dose radiation. HH is a fairly common inherited disorder that causes the body to absorb and store too much iron, and strains of mice with the same genetic defect are being used in this study. Two objectives are to determine whether these mice have greater sensitivity to radiation-induced cancers and to determine whether this sensitivity depends on the accumulation of iron. If higher sensitivities are detected at high-radiation exposure levels, an effort will be made to identify thresholds in the dose-response relationships at low exposure levels.

Communication of Research Results

A goal of the Decision Science Research Institute project (69904) is to establish risk communication as an integral part of the decision process involved in establishing public policies related to cleanup of sources of low-dose radiation. The focus of their research will be understanding individual, group, and community responses to radiation risks. A set of questionnaires was designed to examine attitudes about radiation exposure, the relationship between respondent worldviews and risk perceptions, the role of emotions, and how media stories influence perceptions. Ongoing work will examine the community level context for radiation risk perceptions using the framework of the Social Geography of Risk Communication. Community studies address the social, political, and economic context and the resulting influence on societal responses to low-dose radiation exposures. Other studies will attempt to understand how science information is viewed, evaluated, understood, and applied to low-dose radiation conditions.

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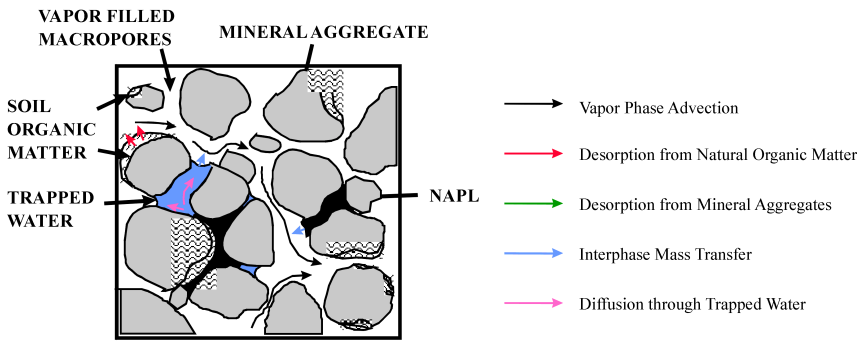
SUBSURFACE CONTAMINATION – DENSE NONAQUEOUS PHASE LIQUIDS

SIGNIFICANT NONAQUEOUS PHASE LIQUID CONTAMINATION IS PRESENT AT ALMOST EVERY MAJOR U.S. DEPARTMENT OF ENERGY SITE

Chlorinated solvents were released into the environment in massive quantities between 1950 and the early 1980s. A small pool of dense nonaqueous phase liquids (DNAPLs) can contaminate a very large volume of water while being difficult to locate, so there is widespread interest in finding geophysical techniques for locating DNAPLs without using numerous boreholes. One EMSP investigation is based on the hypothesis that the complex electrical resistivity of the subsurface will change as the DNAPL concentration changes, so the method is being studied for use as a monitor for remediation activities. Another study is investigating the applicability of ground-penetrating radar for detection of organic liquids in the subsurface, and researchers are conducting field experiments at U.S. Department of Energy (DOE) and U.S. Department of Defense (DOD) sites with known contamination. Another effort is directed toward taking a highly sensitive analytical technique from the research laboratory into a practical, fieldable instrument that could be deployed down-well or in a cone penetrometer for the detection of traces of organic contaminants.

Two studies are working on factors that affect the migration of nonaqueous organic materials in the subsurface. One is exploring the role that naturally produced surfactants may play in the migration of these materials, and another is exploring the vadose zone factors that limit the effectiveness of soil vapor extraction for removing DNAPL contamination from the subsurface.

Factors related to the use of a *Pseudomonas* strain for bioremediation of chlorinated hydrocarbons are being studied in two projects. One group is exploring use of anaerobic biodegradation in regions near DNAPL plumes, and they are also investigating the molecular biology involved in the reactions. Another group is working with the same microorganism, but the focus of their study is on the vadose zone characteristics that are important for the ability of the strain to colonize a region from a single injection point.



Factors that Limit the Effectiveness of Soil Vapor Extraction
This schematic, provided by a University of Illinois project (70045), illustrates the various processes that control the removal of volatile organic chemicals from the vadose zone during soil vapor extraction (SVE). The researchers hypothesize that at sites like Hanford, dry vapor can be pulled into the ground and affect the soil water content during SVE. Consequently, the controlling processes may change with time.

PROBLEMS/SOLUTIONS

- An STCG Needs Statement (SR00-3017) reflects a need that could be stated for every major DOE site: "Technologies, that are non-invasive and prevent cross-contamination, are being sought to determine the concentration of specific contaminants present at the SRS." Two EMSP projects are working on noninvasive methods to satisfy this need.
- An STCG need (OK99-22) stated for a site at Lawrence Livermore National Laboratory is also applicable to every site with DNAPL contamination: "An increased understanding of chlorinated volatile organic compound plume behavior in various hydrogeologic settings is needed to support remediation strategy decision-making." Among many relevant EMSP projects, one is working on unraveling the effects of surface-active materials on DNAPL migration.

ANTICIPATED IMPACT

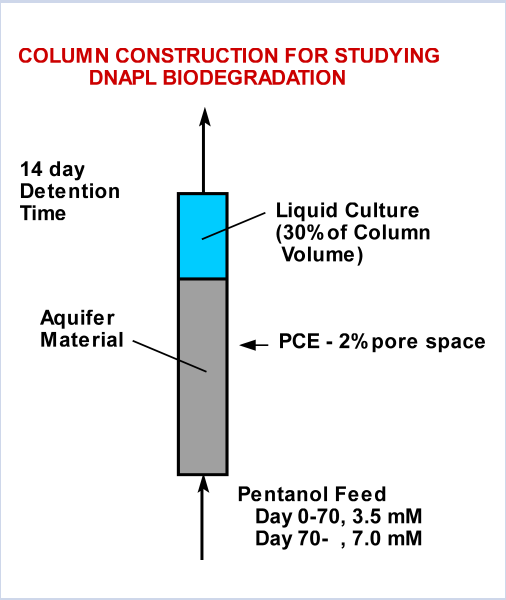
- At current drinking water standards of five parts per billion, one gallon of tetrachloroethylene can contaminate 300 million gallons of water. Thus, techniques for location and remediation of concentrated DNAPLs in the subsurface can save years of pump-and-treat operations.
- Fundamental research in geophysical techniques for locating DNAPLs in the subsurface could lead to substantial long-term savings because every well that does not have to be drilled to locate contaminants saves up to $20,000.
- Microorganisms that can convert chlorinated organic compounds to inorganic chloride and nonhazardous organic materials are known, but large-scale, practical bioremediation of contaminated sites requires a thorough understanding of the factors that enable these organisms to thrive. Successful application of bioremediation procedures would offer very great reductions in cost for remediation of DNAPL plumes as compared to existing removal methods.

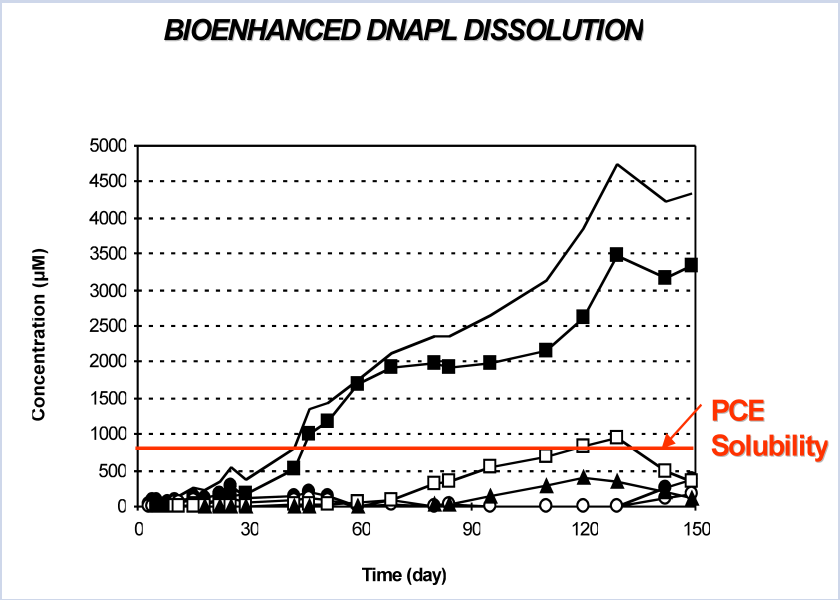
Characterization and Monitoring of DNAPLs in the Vadose Zone

Complex Electrical Resistivity Measurements. Researchers in a New England Research project (70012) are working on the use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface. The work is based on the hypothesis that as organic compounds are removed from the subsurface, the complex resistivity will change. The measured quantity is the phase angle between the applied sinusoidal current applied with two electrodes and the voltage produced in two other electrodes mounted in the sample. Early work on this project involved developing a system that could resolve complex resistivity phase angles of a milliradian over the frequency range of 0.001 to 100,000 Hertz. Because of variable moisture levels, a challenge for field measurements will be to distinguish changes in DNAPL concentrations from other changes in the system.

Ground-Penetrating Radar for Detection of DNAPLs. A University of Wyoming project (70052) is directed toward the use of ground-penetrating radar (GPR) for direct detection of DNAPLs. This project focuses on three aspects of reflected wave behavior—propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Field experiments are being conducted at the Savannah River and Hanford sites as well as at five DOD sites. The first survey was conducted at a shallow DNAPL zone at Savannah River, and extensive efforts were being made to correlate the GPR data with information available from direct measurements made using a cone penetrometer. Other field experiments either in progress or completed include a controlled tetrachloroethylene injection experiment at Dover AFB, an experiment to detect jet fuel at Hill AFB in Utah, and DNAPL detection in the vicinity of a carbon tetrachloride crib at Hanford. Other experiments over known contaminated sites will occur at three additional air force bases in Michigan and California.

Sensitive REMPI Methods for Detection of Organic Vapors. There are currently no *in situ* methods for measuring low levels of organic vapors of the type that would be indicative of subsurface contamination in the vadose zone. High concentrations of organic compounds can be detected with Raman spectroscopy, for example, and a few compounds can be detected by their fluorescence properties. The goal of a University of South Carolina/LLNL project (70050) is to develop a resonant enhanced multiphoton ionization (REMPI) system that can be deployed in a cone penetrometer for the sensitive detection of species such as carbon tetrachloride that cannot be detected by fluorescence techniques. Their team includes persons with expertise in analytical spectroscopy, hydraulic measurements and cone penetrometers, electrical engineering with expertise in optical parametric oscillator design, and fiber optics. They have demonstrated measurements of low parts-per-billion levels of toluene, and they are designing new REMPI probes that use visible lasers to reduce the cost and complexity of the instrumentation.





Anaerobic Biodegradation near DNAPL Plumes

A Stanford University project (70063) exploring use of anaerobic biodegradation in regions near DNAPL plumes has found that certain dehalogenating microorganisms can decompose tetrachloroethylene, trichloroethylene, and other chlorinated ethenes at concentrations near saturation in water. Above: Biological enhancement of tetrachloroethene (PCE) dissolution shown in a soil column with 2% residual PCE saturation and fed a solution containing up to 7 mM pentanol as electron donor. Effluent concentration of PCE (●), TCE (○), cDCE (■), VC (□), ethene (♦), and the total (without marker).

Effects of Surface-Active Materials on DNAPL Migration. The distribution of DNAPLs within the vadose zone is affected by heterogeneities in the porous matrix and by the interfacial properties that determine the interactions among different solid and liquid phases. Small amounts of surfactants can have large impacts on the interactions of immiscible fluids, such as oil and water, so it would be reasonable to expect that surface-active chemicals present in the vadose zone could have a considerable effect on the migration of DNAPLs. Surface-active materials can be produced through microbial metabolic processes, and the goal of a Clarkson University/WSRC project (70035) is to understand the effects of various interfacial phenomena on the accessibility and migration of DNAPLs in the vadose zone. One objective is to identify the presence of surface-active materials and to quantify interfacial properties in an actual DNAPL plume at Savannah River Site. Other objectives include identifying how DNAPL-metabolizing cultures affect interfacial properties and quantifying the effects associated with DNAPL surface chemistry on flow in the vadose zone.

Factors that Limit the Effectiveness of Soil Vapor Extraction. The aim of a University of Illinois project (70045) is to gain a better understanding of the processes that limit the effectiveness of soil vapor extraction (SVE) for the removal of DNAPLs from heterogeneous porous media typical of the vadose zone. Sorption isotherms and desorption kinetic profiles will be measured for silica gel and sand at various humidities, incubation times, and DNAPL concentrations. The location and size of individual pores containing DNAPLs, water, and vapor in flow-through columns filled with either model or natural sediments will be determined using magnetic resonance imaging. Imaging results will be used along with modeling techniques to describe the transient distribution of phases as a function of time and location. These relationships will be used in a transport model to evaluate how different processes affect SVE performance in practical applications.

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Bioremediation

Anaerobic Biodegradation near DNAPL Plumes. Solvents such as carbon tetrachloride or trichloroethylene have low mutual solubilities with water, so these materials tend to remain segregated as concentrated liquids in the subsurface. Biodegradation of these DNAPLs was previously thought not to be possible because of toxicity to microorganisms, but a Stanford University project (70063–a renewal of 54666) is exploring the use of anaerobic biodegradation in regions near DNAPL plumes. They have found that certain dehalogenating microorganisms can decompose tetrachloroethylene, trichloroethylene and other chlorinated ethenes at concentrations near saturation in water. These solutions are inhibitory to other naturally occurring organisms so they did not compete for the electron donor required for the reaction. The group is attempting to provide a molecular understanding of the biological mechanisms involved in the reactions and to determine the cellular components involved in carbon tetrachloride transformation by a *Pseudomonas* strain without the formation of chloroform.

Factors that Affect Microorganism Colonization in the Subsurface. The lack of knowledge about how physical and hydrologic features of the vadose zone control the spatial distribution of microbial activity and the potential for microorganisms to colonize this region create uncertainties about the practicality of deep vadose zone bioremediation. A PNNL/Oregon State University project (70165) is also exploring the use of the same *Pseudomonas* strain for DNAPL remediation as described in the previous project, but the focus of this project is on the ability of strain KC to colonize sediment from a single inoculation point as a function of vadose zone characteristics, such as water-filled porosity, pore throat size, aqueous nutrient concentration, and distance from a nutrient injection point. The impact of several other vadose zone hydrological processes on colonization will also be studied. In addition, researchers in this project are modifying a widely used computer program for vadose zone flow and transport modeling to include coupled biological and hydrologic processes.

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Office of Science & Technology
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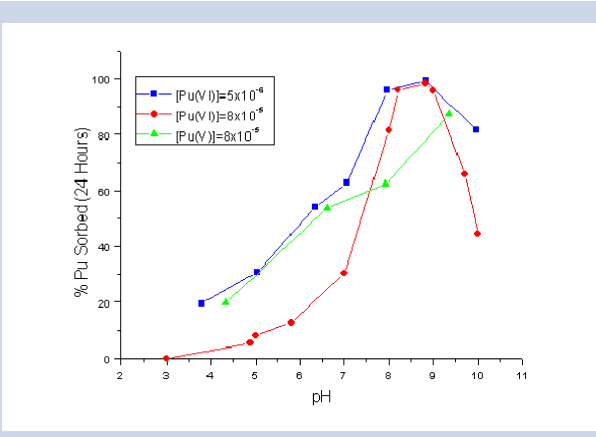
LOCATION AND TRANSPORT OF METALS AND RADIONUCLIDES IN THE SUBSURFACE

DISCOVERY OF MORE RAPID MIGRATION OF RADIONUCLIDES THAN EXPECTED HAS LED TO A GREATER EFFORT TO INTEGRATE SUBSURFACE SCIENCE INTO CLEANUP ACTIVITIES

The projects described here involve either analytical determinations of radionuclides or studies related to the mechanisms by which metal ions migrate away from the original site of contamination.

An innovative analytical technique was developed by one EMSP research group to incorporate scintillating materials into extraction chromatographic separation materials so that alpha- and beta-emitting radionuclides could be both separated and detected with high sensitivity. Another project was directed toward developing a selective sensor for detection of pertechnetate ions in complex mixtures.

Understanding the fate and transport of radionuclides is essential for rational design of remediation efforts. Two projects are exploring how the formation of colloids affects the transport of plutonium and other radionuclides in the subsurface, and one of these has developed ways to determine the colloidal species actually present in groundwater with very low levels of contamination. Several studies are investigating the effects the highly alkaline fluids that have leaked from the Hanford tanks may have on radionuclide transport. One project has obtained core samples like those under the tanks, and these samples are being used for transport experiments. Another group has studied the sorption of radionuclides on clays that have been in contact with highly alkaline solutions, while another is focused on a mechanistic understanding of how tank fluids migrate through the vadose zone.



Transuranic Interfacial Reactions on Manganese Oxide/Hydroxide Minerals
The objective of a LBNL/PNNL project (70176) is to provide information about the interactions of plutonium and neptunium with manganese-containing minerals. Above: Sorption of Pu(VI) and Pu(V) on manganite (MnOOH) as a function of plutonium concentration and pH. The point of zero charge of manganite (the point where the mineral surface is electrically neutral) occurs at a pH of 6.4. At pH values greater than this, the surface has a net negative charge, resulting in a larger amount of Pu sorbed onto the surface.

Studies of interactions of radionuclides with specific components of the subsurface include two studies of the interaction of various radionuclides with carbonate coatings on minerals and how these interactions may affect transport. Another project is making a detailed study of the silica oligomers that can form in highly basic solutions and the complexes they can form with various radionuclides. Another study is directed toward understanding interactions of plutonium and neptunium with manganese minerals that are present at low levels at some U.S. Department of Energy (DOE) sites.

PROBLEMS/SOLUTIONS

- STCG Need RL-SS14 points out that radioactive contaminants requiring improved field detection sensitivities include uranium, plutonium, strontium-90, and technetium-99. A novel system based on the incorporation of scintillating materials into extraction chromatographic separation beads has already been demonstrated to have sufficient sensitivity for technetium-99 groundwater monitoring, and similar work is underway to develop systems for strontium-90 and actinide determinations.
- Although many radionuclide contaminants are present at very low levels at various DOE sites, some common contaminants include plutonium, strontium-90, cesium-137, various isotopes of uranium and rare earths, tritium, thorium, technetium-99, radium, and potassium-40. Either the detection or migration of most of these species is being investigated in EMSP projects awarded in 1999.

ANTICIPATED IMPACT

- As described in an STCG Need Statement (ID-S.1.10), “migration of plutonium to sedimentary interbeds underlying buried waste at some Idaho sites has apparently occurred at a rate much faster than could be predicted by solute transport processes. Plutonium has been determined in laboratory studies and field sampling programs to form colloids in water. These colloids are not reactive with exchange sites on rocks and minerals and have the potential to migrate at essentially the same rate as the water moving through the vadose zone.” Two EMSP projects are working on understanding how these colloids can form and which are present at some DOE sites.
- About 350 billion gallons of radionuclide-contaminated water were intentionally discharged into the ground over the years of weapons production, and at least a million gallons of much more concentrated solutions have leaked from high-level storage tanks. Recent detection of radionuclides in the groundwater beneath some high-level tanks has made more reliable predictions of transport a high priority.

Analytical Determinations of Metals and Radionuclides in the Subsurface

Scintillating Microspheres for Radionuclide Detection. Alpha- and beta-emitting substances in water are difficult to detect because of the short ranges of the emitted particles in water. A PNNL/Clemson University group (70179) has developed a novel system for the detection of radionuclides such as strontium-90, technetium-99, and actinides. The system is based on the development of selective scintillating microspheres (SSMs). Thus, the ion of interest is selectively bound to the microspheres. The SSMs, however, also contain scintillating materials that emit light when an alpha- or beta-emitting substance is on a nearby location in the bead, and a photomultiplier or diode sensor can then be used to detect the emitted light. This system has been used to detect technetium in water at concentrations below the maximum permissible drinking water level, and work continues on developing systems for the selective detection of strontium-90 and actinides.

Pertechnetate Sensor. Analysis of any substance in a complex mixture is difficult because most sensors will respond to many species. A University of Cincinnati/PNNL group (70010) is developing a sensor for technetium based on the same general concepts that they used in a previous project (54674) to develop a sensor for ferrocyanide. A chemically selective film is coated onto an optically transparent electrode. Even though the film cannot bind a particular ion exclusively, it can be chosen to show selectivity for pertechnetate ions. Then the pertechnetate ion will be reduced electrochemically and converted into a technetium coordination compound that gives a strong optical signal. Therefore, to be detected, a species must be incorporated into the film, be reduced at the potential used for the electrochemical process, and then form an absorbing substance at the wavelength used for the optical detection. This threefold selectivity may enable reliable detection of pertechnetate without the usual elaborate separation procedures required for conventional analyses.

Transport of Metals and Radionuclides in the Vadose Zone

Colloid Facilitated Transport of Radionuclides. Radionuclides, such as plutonium and cesium, have been detected under the Hanford tanks at much greater depth than predicted by current theories of vadose zone contaminant transport. It has been suggested that the mobility may be higher than expected because of colloid-facilitated transport through the vadose zone, and a Washington State University project (70135) is designed to investigate this possibility. The first objective is to determine the characteristics of the colloidal particles that form under conditions similar to those found when Hanford tank liquids leak into the vadose zone beneath the tanks. Next, the interactions between colloids, contaminants, and the soil matrix will be studied under various ionic strength and pH conditions, and the mobility of colloids through the soil will be evaluated. Preliminary experiments have shown that a considerable amount of colloidal particles can be mobilized when a concentrated salt solution infiltrates the Hanford sediments and is subsequently diluted.

Studies with Core Samples from Hanford
The goal of an ORNL/PNNL/Stanford University project (70219) is to provide an improved understanding and predictive capability for the fate of the radionuclides that have leaked from the Hanford tanks. In their work, as illustrated here, undisturbed sediment cores of material similar to that beneath the Hanford tank farms were acquired with a rotary coring apparatus that could obtain cores at any angle within the formation. Both horizontal and vertical cores were obtained, and the fate and transport of radionuclides at different water contents were investigated.

Speciation, Mobility, and Fate of Actinides in Groundwater. A Woods Hole Oceanographic Institute/PNNL project (70132) is designed to gather fundamental data essential for predicting the migration of plutonium in an aqueous environment and is a continuation of a previous project (54683) that also addressed this issue. The researchers collect samples using a technique that allows them to separate species in solution from colloids. Samples for ascertaining redox properties are separated immediately in the field. They determine the isotopic ratios using the high sensitivity of thermal ionization mass spectrometry, with subfemtogram detection limits. They used these techniques to show that Pu in the groundwater at Savannah River Site (SRS) originates from both weapons grade Pu and from a more mobile curium precursor. Most of the Pu at SRS is in an oxidized form that is more mobile than most standard models predict. Current work involves extensive sampling at Hanford to assist in the prediction of the migration potential. The main focus remains on identifying the Pu species present at Hanford, the mobility of these species, and the role that colloidal materials play in Pu transport.

Studies with Core Samples from Hanford. The fate and transport of radionuclides beneath the Hanford tank farms are also the subject of an ORNL/PNNL/Stanford University project (70219). They obtained undisturbed 0.3 meter x 0.3 meter cores by both horizontal and vertical sampling in a Hanford location similar to those under the tank farms, so they can duplicate field conditions. Preliminary results suggest that lateral flow beneath the tank farms is a strong contributor to the spread of contaminants and that uranium is strongly bound to the various sediments beneath the tank farms. The transport of cesium, technetium, and uranium radionuclides will be studied in a manner that will isolate hydrological and geochemical mechanisms that are important at different water contents. In addition to the macroscopic fate and transport experiments, interfacial molecular techniques will be used to quantify the distribution and chemical environments of the sorbed contaminant species. The goal is to provide an improved understanding and predictive capability for the fate of the radionuclides that have leaked from the Hanford tanks.

Sorption of Radionuclides on Altered Clay Surfaces. Few studies have been conducted to study the sorption of radionuclides on clays at the extreme conditions expected when highly concentrated basic solutions leak from high-level storage tanks into the subsurface. The focus of a Pennsylvania State University/BNL/PNNL study (70126) is on the sorption and release of cesium and strontium on clay surfaces that have been altered by exposure to solutions similar to those in the high-level tanks. They have studied the extent of the sorption of Cs and Sr on a variety of purified clay samples, both before and after exposure to a synthetic tank waste simulant solution. Sorption studies on a variety of clays have shown that the extent of Sr sorption is higher than for Cs, as expected, and strongly controlled by secondary mineral formation and short-range-ordered phases that evolve with increasing reaction time. Major efforts are being made to characterize the coordination environment of the sorbed ions. Their results are intended to be applied in equilibrium and transport models for radionuclide distribution between solid, colloidal, and dissolved phases.

Effects of Tank Leaks on Subsequent Flow and Transport. A University of Colorado/PNNL project (70070) is focused on obtaining a mechanistic understanding of how tank fluids migrate through the vadose zone, and they are particularly interested in how leaks of tank liquids will cause changes in porosity and permeability that will affect flow paths of subsequent leaks. The tank solutions have high concentrations of various salts, high pH, and high aluminum concentrations, which can significantly alter the vadose zone sediments by dissolution of primary minerals and precipitation of new minerals. Their first goal is to obtain kinetic rate laws for the dissolution of quartz and feldspar, as well as the precipitation of secondary phases, when tank liquids contact them. They will attempt to obtain an understanding of the nucleation mechanisms, nucleation sites on soil minerals, and the role of reactive surfaces on dissolution and precipitation reactions.

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Interactions of Radionuclides with Carbonate Coatings. Carbonate grain coatings are more abundant in some vadose zone locations than are the oxyhydroxide grain coatings that are usually thought to control the sorption of inorganic ions. The goal of a PNNL/Stanford University/University of Wyoming project (70121) is to understand the interaction of some contaminants (strontium-90, cobalt-60, chromate, and pertechnetate) with carbonate coatings in order to improve forecasts of contaminant migration. Questions being addressed include: (1) Do carbonate coatings form preferentially on particular mineral surfaces? (2) Do carbonate coatings inhibit electron transfer reactions at otherwise reactive surfaces? (3) Do carbonate coatings enhance the binding of species such as ^{90}Sr and ^{60}Co? The rate of dissolution of carbonate coatings has been shown to be enhanced by the presence of certain impurities, and this could be important for understanding the stability of contaminant-containing carbonate surfaces.

Factors that Affect Carbonate Uptake of Contaminants. The objective of a State University of New York–Stony Brook/PNNL project (70146) is to assess the role of calcium carbonate in the uptake and retention of inorganic contaminants, such as cobalt, cesium, lead, strontium, and chromium. Their work includes detailed microscopic and spectroscopic characterization of carbonate coatings and caliche along with studies of the factors that influence uptake behavior and retention behavior. Early work showed that the detailed structure of the carbonate surface controls the extent to which chromate is removed from vadose-zone fluids. Similar work is exploring uranyl uptake on carbonate surfaces. They have also studied the interaction of lead and strontium ions with natural caliche samples, and they have shown that only a small fraction of the caliche surface offers favorable reaction sites for lead uptake. X-ray absorption fine structure spectroscopy and X-ray fluorescence techniques are being used to characterize the binding of various metal ions to carbonate surfaces.

Thermodynamics of Radionuclides in Highly Basic Solutions. A PNNL/Florida State University project (70163) is working on the thermodynamics of the species formed by radionuclides in highly basic solutions, particularly those with high silica concentrations. Silica can form monomers, dimers, and higher oligomers in highly basic solutions, and each of these species has unique binding capabilities with different radionuclides. These complexes may result in more highly soluble and mobile species of radionuclides than would be anticipated from the initial composition of the vadose zone minerals. Their work includes experimental determinations of the species present in solution, molecular simulations to help identify species structures, and physical chemistry measurements to obtain the thermodynamic data necessary for predicting contaminant complexation and waste neutralization reactions. Their efforts are particularly directed toward reactions of strontium, cobalt, americium, uranium, technetium, and thorium ions in these complex solutions.

Transuranic Interfacial Reactions on Manganese Oxide/Hydroxide Minerals. The objective of a LBNL/PNNL project (70176) is to provide information about the interactions of plutonium and neptunium with manganese-containing minerals. Even though these minerals are typically minor phases in the vadose zone, they may preferentially sorb plutonium and other transuranics over the much more prevalent iron oxide minerals. Sorption experiments have been performed on several manganese-containing minerals to determine both the rate and the extent of the sorption. The data for plutonium sorption on manganite (MnOOH) show that independent of the initial oxidation state (VI or V) the plutonium is completely taken up by the mineral at pH 8.6, thus immobilizing the radionuclide contaminant. Above and below this pH, the uptake decreases steadily to 0% at pH 3 and about 40% at pH 10. Hausmannite (Mn_3O_4) shows even better plutonium uptake under the same conditions. A combination of X-ray absorption fine structure spectroscopy and optical absorption spectroscopy showed that the plutonium sorbed onto the minerals is present as Pu(IV). This implies that the minerals reduce the high oxidation state plutonium in solution (VI and V) to insoluble tetravalent plutonium, which then sorbs onto the mineral surfaces. The plutonium remaining in solution at the pH values where incomplete uptake occurred was present as Pu(V). The thermodynamic and kinetic parameters obtained from these experiments will be used as input data for reactive transport modeling in the vadose zone.

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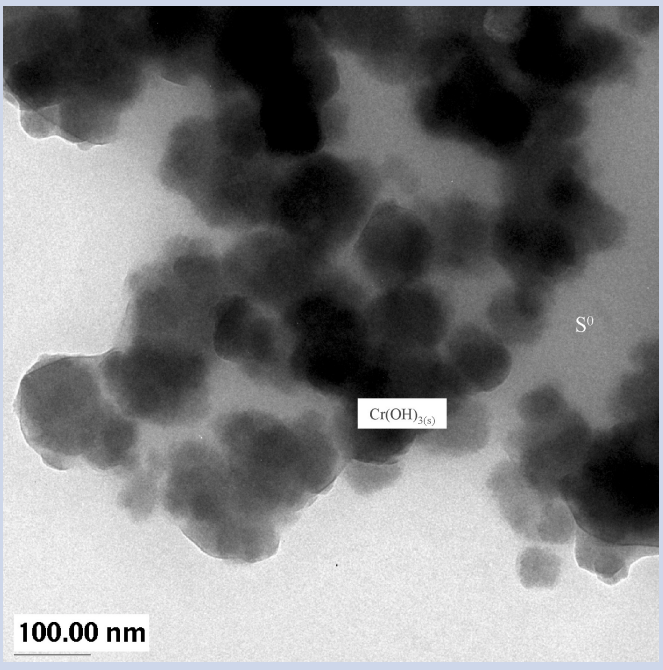
STABILIZATION AND TREATMENT OF METALS AND RADIONUCLIDES IN THE SUBSURFACE

Conversion of metals and radionuclides to less mobile species is the only practical remediation strategy at many sites

This fact sheet is the second of two that summarize 1999 EMSP projects that are related to the U.S. Department of Energy (DOE) Subsurface Contaminants Focus Area (SCFA) Metals and Radionuclides Product Line. Two of these projects are closely related to the fate and transport issues considered in the first fact sheet, but they deal more directly with specific interactions that can result in immobilization of species in the subsurface. One is exploring reactions of pertechnetate ions that can occur on certain iron-containing minerals, while the other is focused on understanding the interactions of various radionuclides with the new materials that are formed by reactions of highly alkaline fluids with minerals under the Hanford tanks.

Two other projects involve methods for inducing chemical reactions in the subsurface that convert a more mobile metal species in solution into a less mobile solid form. One of these is exploring the injection of urea into aquifers that contain organisms that will hydrolyze it to form ammonium carbonate, which will form calcium carbonate precipitates that can trap low concentrations of other radionuclides that were in solution. The injection of hydrogen sulfide gas into the subsurface to form insoluble sulfides with more mobile metal species has been explored by projects in the SCFA, and an EMSP project is investigating fundamental issues related to this potential method for chromate remediation.

A study of the use of genetically engineered plants to remove mercury from soils is being continued from a previous project, with current work focused on understanding the molecular biology of this phytoremediation process. Similar techniques could perhaps be used to develop plants to accumulate other heavy metals.



***In Situ* Gaseous Reduction**
A New Mexico Institute of Mining and Technology/PNNL project (70088) is exploring the potential use of gaseous hydrogen sulfide, H_2S, to convert chromium(VI) and other hazardous metal ion species into insoluble compounds with low mobility. Chromate reduction by hydrogen sulfide produces less mobile $Cr(OH)_{3(s)}$ (dark area) and S^0 (bright area), as analyzed by Transmission Electron Microscopy (TEM) and associated Energy-Dispersive X-ray Spectroscopy (EDS).

Problems/Solutions

- "The primary technical gap associated with describing and quantifying the solubility of contaminants is that there is an insufficient understanding of solubility of selected contaminants in various waste matrices (e.g., technetium in tank waste) and how this solubility then changes as the waste interacts with the vadose zone sediments at the interface" (STCG Need RL-SS14). One project is focused on developing an understanding of the solubility of technetium in contact with iron-containing minerals in the vadose zone.
- An STCG Need, Transport of Contaminants (RL-SS26-S), cites a need for "geochemical models for the incorporation of trace contaminants (metals, radionuclides) into secondary phases via co-precipitation." A project that is exploring potential methods to induce calcium carbonate precipitation for removing certain radionuclides from groundwater may also contribute information useful for understanding natural processes that stabilize radionuclides.

Anticipated Impact

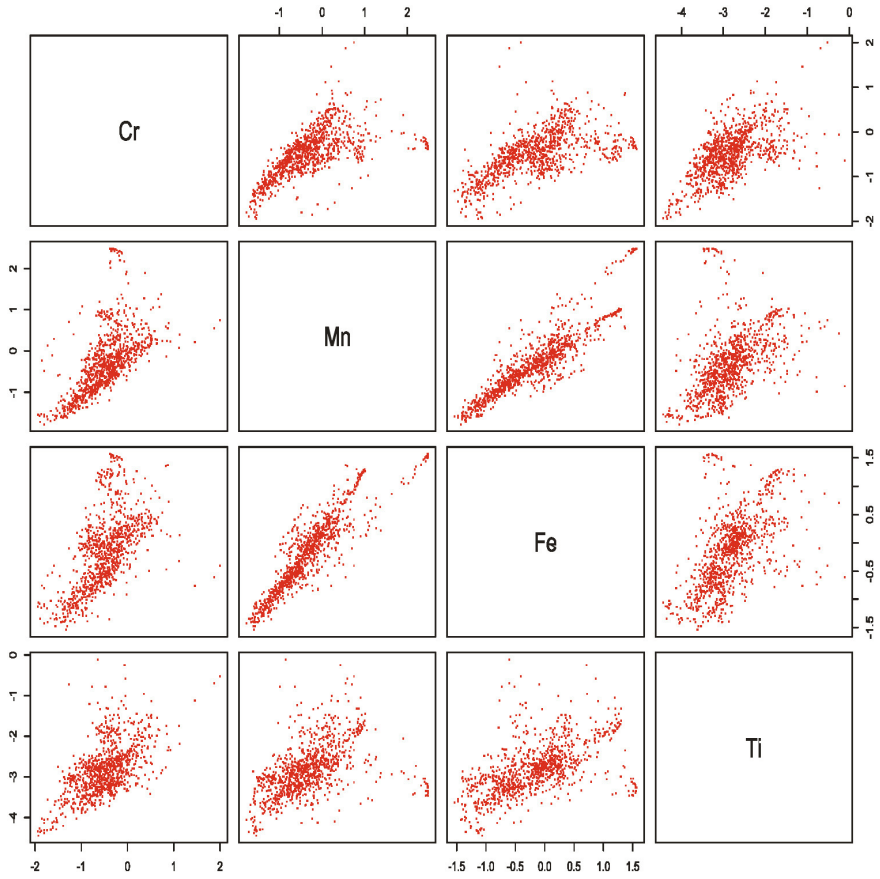
- An estimated 240,000 to 470,000 pounds of elemental mercury were discharged at the East Fork Poplar Creek site at Oak Ridge as a result of a lithium separation process at the Y-12 Plant, and several other DOE sites have substantial mercury pollution problems. Although direct physical and chemical remediation processes may be useful at sites with very high mercury levels, genetically engineered plants produced in an EMSP project may provide a less expensive means for remediating lower levels of mercury from contaminated soils.
- To illustrate the magnitude of the cleanup problem, there are 35 Project Baseline Summaries for the Hanford site alone, and one of these (300 Area Remedial Action) cites 240 waste sites, many of which have radionuclide contamination. Retrieval of the contaminants from all contaminated sites is not feasible, so methods to stabilize radionuclides in their current location may offer the best solution for most sites.

Technetium Mobility in the Vadose Zone. More than 900 curies of technetium were discharged into the ground at Hanford. Technetium is easily oxidized to form the highly soluble and mobile pertechnetate species, but reduction reactions on iron(II)-containing mineral surfaces could result in forming technetium dioxide and other reduced species with much lower mobility. These processes are the focus of a PNNL/LANL project (70177). Their strategy is to develop a description of the reduction of pertechnetate ions on iron(II)-containing minerals, to determine the stability of the resulting reduced technetium solids, and to use contaminated Hanford sediments to validate their models of technetium mobility in the vadose zone. The goal is to be able to ascertain which sites pose the greatest environmental threat.

Impact of Alkaline Tank Fluids on Radionuclide Immobilization. The Ohio State University/PNNL/Stanford University project (70081) is directed toward understanding how the most common radionuclides might become immobilized in the subsurface solids that have been impacted by alkaline tank fluids. The effect of aging on the stability of complexes on solids formed from neutralization and nucleation of alkaline aluminate solutions is being investigated, and the sorption or co-precipitation of various radionuclides in the solids formed by reactions of alkaline aluminate solutions with various minerals and with Hanford sediments is being studied. They have shown that addition of amorphous silica to alkaline sodium aluminate solutions forms solids that are much more effective at removing cesium from solution than were the solids formed in the absence of the silica. They also plan to use a variety of modern instrumental methods to characterize the chemical forms of the species present in actual core samples taken from underneath the SX-108 tank.

Chemical Treatment of Metals and Radionuclides in the Subsurface

In Situ Formation of Calcium Carbonate for Radionuclide Immobilization. An INEEL/Portland State University/University of Toronto project (70206) is directed toward development of an *in situ* formation of calcium carbonate to remove certain radionuclides from solution. The idea is to inject urea into a contaminated aquifer. If urease-containing organisms are present, the urea will be hydrolyzed to form ammonium carbonate, which will react with low concentrations of calcium to form calcium carbonate and trap other metal ions in the precipitate. Urea is inexpensive and poses no environmental



Impact of Alkaline Tank Fluids on Radionuclide Immobilization

An Ohio State University/PNNL/Stanford University project (70081) is directed toward understanding how the most common radionuclides might become immobilized in subsurface solids that have been impacted by alkaline tank fluids.

This graph shows correlations of the spatial distributions between Cr, Mn, Fe, and Ti for a borehole sample under tank SX-108. Data were collected on the undulator beam line at GSECARS Sector 13 (Advanced Photon Source, Argonne National Laboratory) using X-ray micro-fluorescence elemental mapping technique. The x-axis represents the logarithm of the normalized fluorescence intensity of the element in each column. The y-axis corresponds to the log intensity of each element.

X-ray absorption spectra (XAS) collected at beam line 11-2 of the Stanford Synchrotron Research Laboratory indicate that most of the Cr in the sediments beneath SX-108 remains as the more mobile Cr(VI). However, sediments samples with pH values in excess of 9 did show a dominance of Cr as Cr(III). Companion laboratory studies suggest that some Cr(VI) was reduced to Cr(III) *in situ*, by reactions with Fe(II) present in alumino-silicate clays, magnetites, and illmenites.

hazard, so it could be injected into aquifers. Early results indicated that the potential for using urea hydrolysis as the basis for an *in situ* remediation technique for strontium-90 and other divalent metal ions is promising. Urea-hydrolyzing bacteria were found in the Snake River Plain Aquifer at INEEL, and it was found that these bacteria can catalyze the formation of calcite. An experiment to test this procedure in a groundwater well at INEEL is being planned, and the group is also exploring the feasibility of this technique to remediate a strontium plume at the Hanford 100 area.

In Situ Gaseous Reduction. Unlike organic chemicals, metal ions in the subsurface cannot be destroyed. However, more soluble and mobile species, such as chromate, can be converted into insoluble, less mobile, and therefore less hazardous forms. A New Mexico Institute of Mining and Technology/PNNL project (70088) is exploring the potential use of gaseous hydrogen sulfide, H_2S, to convert chromium(VI) and other hazardous metal ion species into insoluble compounds with low mobility. If H_2S is injected into the soil, what will be the effect of mineral surfaces on the rate of reduction of chromate or on the rate of oxidation of H_2S by air? What other minerals in the subsurface will also react with the H_2S, making it unavailable for the desired reaction? If chromium(VI) is reduced to chromium(III) by H_2S in the subsurface, what is the long-term resistance to reoxidation to the more mobile Cr(VI)? What variables in soil water chemistry can affect the reduction reaction? These and other related questions are being addressed in laboratory studies, and tests are being conducted with Hanford soil samples to define reaction parameters for the Cr(VI)-H_2S-oxygen-soil system.

Project Teams

Lead Principal Investigator (Award Number)

- University of Georgia
  PI: Richard B. Meagher (70054)
- Ohio State University
  PI: Samuel J. Traina (70081)
  Pacific Northwest National Laboratory
  Stanford University
- New Mexico Institute of Mining & Technology
  PI: Baolin Deng (70088)
  Pacific Northwest National Laboratory
- Pacific Northwest National Laboratory
  PI: Nancy J. Hess (70177)
  Los Alamos National Laboratory
- Idaho National Engineering & Environmental Laboratory
  PI: Robert W. Smith (70206)
  Portland State University
  University of Toronto

Phytoremediation of Heavy Metals from Soils

Use of Plants for Removal of Mercury from Soils. Several DOE sites, particularly the Oak Ridge National Laboratory, have areas with significant levels of mercury contamination. A University of Georgia project (70054) is continuing work from a previous project (54837) to demonstrate that native trees, shrubs, and grasses can be engineered for remediation of mercury-contaminated sites. This group has engineered several plants to express two bacterial genes, *merB* and *merA*. Plants expressing *merA* extract and reduce ionic mercury to metallic mercury which is transpired from the leaves, and those expressing *merB* extract highly-toxic methylmercury from the soil and degrade it to ionic mercury. Current work is focused on obtaining a detailed understanding of the mechanisms by which these plants process the various forms of mercury in order to improve the phytoremediation designs. In addition, attempts will be made to produce plants to accumulate mercury so that it can be removed by harvesting the plants rather than by vaporizing it into the environment. Presumably, similar techniques could be used to design plants to hyperaccumulate other heavy metal pollutants.

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SUBSURFACE CONTAMINATION – SUBSURFACE SCIENCE AND SOURCE TERM CONTAINMENT

A MAJOR OBJECTIVE OF THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM IS TO GENERATE NEW KNOWLEDGE TO SUPPORT CLEANUP OF SUBSURFACE CONTAMINATION

The Source Term Containment and Remediation product line in the Subsurface Contaminants Focus Area (SCFA) addresses the development of containment and stabilization methods to prevent the spread of contaminant plumes, particularly from former landfills, disposal areas, and trenches. Most of the EMSP projects summarized here are applicable to this area because knowledge of the characteristics of the subsurface is a prerequisite for the treatment, confinement, and stabilization of subsurface contamination. Many of these projects, however, involve investigations of fundamental subsurface science and so are of general interest to all areas of the SCFA.

It is not possible for the most sophisticated modeling programs to make reliable predictions of contaminant migration in the subsurface without detailed information about characteristics such as porosity, permeability, and moisture level. Geophysical techniques being explored to provide some of this information include seismic methods, cross-borehole and ground-penetrating radar, high-frequency electrical impedance methods, electrical resistance tomography, and others in combination with hydrogeological measurements. Several of these projects involve controlled laboratory experiments, while others have set up large-scale experiments in well-characterized, heavily instrumented facilities to provide better understanding of how measured geophysical parameters are related to known changes in subsurface parameters.

The heterogeneity of the subsurface characteristics at many of the arid sites with major contaminant problems presents severe problems for fate and transport modeling. EMSP projects include efforts to improve experimental and modeling studies of flow in coarse media, and another effort is directed at combining small-scale direct measurements of soil properties along with geophysical measurements to infer soil properties at unsampled locations. Another project is using an extensively instrumented, large-scale test facility to correlate geophysical and hydrogeological measurements with known contaminant infiltrations. Vertically oriented, permeable structures may provide the most significant pathways for contaminant transport, so another project involves a detailed survey to identify the spacing and thickness of such vertical structures at Hanford.

Vertical Structures and Contaminant Migration
A PNNL project (70193) has conducted a ground-penetrating radar survey to identify spacing and thickness of clastic dikes. Above: Vertical clastic dike cutting layered sediments of the Hanford formation. Measurements are providing data for reactive flow and transport modeling to determine if clastic dikes provide fast paths for fluid transport through the vadose zone.

PROBLEMS/SOLUTIONS

- As stated in an STCG Science Need (ID-S.1.09), "a method or model is needed that will address the effects of space, time, and scale on the mass transport of the solute through differing media." The vadose zone at several major U.S. Department of Energy (DOE) sites contains gravel and gravelly sands, and flow through such materials is not described well by classical models. Both macroscopic and microscopic studies of fluid flow in Hanford sediments are being conducted by an EMSP project to improve predictions for the fate of contaminants in such media.
- As described in *Research Needs in Subsurface Science* (National Research Council, March 2000), "the subsurface characteristics at a site place fundamental controls on contaminant fate and transport behavior. Knowledge gaps include understanding which characteristics control fate and transport behavior in the subsurface and also understanding how those characteristics can be measured at the appropriate scales over large subsurface volumes, using both indirect and direct techniques." Most of the projects described here are directed at closing precisely these gaps in understanding subsurface characteristics.

ANTICIPATED IMPACT

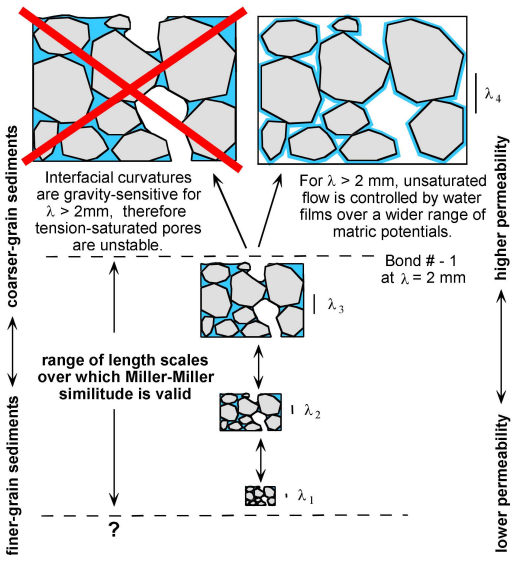
- "The primary technical gap associated with delineating contaminant plumes in the vadose zone is insufficient soil, geophysical, geochemical, and hydrological data or methods to resolve subsurface heterogeneities, characterize geohydrologic properties, and map contaminant distributions at different scales in the vadose zone," (STCG Science Need RL-SS31). A wise use of resources requires that remediation activities occur where the most significant risks occur and that resources not be wasted on sites that do not present tangible risks. Thus, the ability to tell the difference is prerequisite to an effective environmental remediation program.

Geophysical Techniques

Improved Geophysical Imaging. In situ remediation requires information about subsurface porosity, permeability, and fluid saturation, and an LLNL project (70108) is designed to determine the effects of fluid distribution on measured geophysical properties for partially saturated, shallow subsurface conditions. The project is a continuation of a previous project (55411) with the goal of improving geophysical imaging without using expensive, slow-core drilling methods. An ultrasonic apparatus for simultaneous measurement of compressional and shear wave velocities has been modified to enable measurements on partially saturated soil samples, and researchers are continuing testing of a new data analysis method for seismic data that shows how partial saturation affects seismic properties. Thus, controlled laboratory experiments are being used to measure geophysical properties as functions of saturation, pressure, and soil composition, and then rock physics theories will be used to relate these measurements to hydrogeologic properties and to generalize results to the field scale.

Ground-Penetrating Radar for Determining Moisture Content. Contaminant transport in the vadose zone is very dependent on moisture content, so accurate estimates of moisture content are essential for the design of containment or treatment processes. The objective of a Stanford University/University of British Columbia project (70115) is to develop the usefulness of both cross-borehole and ground-penetrating radar methods for the determination of moisture content. Their work is focused on answering two questions: (1) Can a measure of the dielectric constant of a volume of the subsurface be used to determine the moisture content of that volume? and (2) Can the spatial distribution of radar reflections be used to characterize the spatial distribution of moisture content in the subsurface? This work is a combination of laboratory, field, and theoretical studies, all of which are related to improved use of radar methods to characterize moisture content in the vadose zone.

High-Frequency Impedance Methods. High-frequency impedance methods in the 10-Hertz to 1-Megahertz range are sensitive to the amount and composition of fluids present in porous media and are particularly useful for situations in which ground-penetrating radar cannot penetrate to sufficient depths. A SNL/ElectroMagnetic Instruments project (70220) is designed to improve the usefulness of this method. The goal of their work is to produce a combined measurement and interpretation package for noninvasive, high-resolution characterization of larger transport pathways, certain types of contamination, and heterogeneity within the vadose zone. Early work has involved measurements at a well-characterized site in order to test the instruments and methods; future work will be conducted at Hanford site.



Flow and Transport in Coarse Media
An LBNL project (70069) is designed to improve understanding of the flow and transport of contaminants because some aspects of the flow in coarse media are not predictable with classical modeling techniques. Above: Scaling of unsaturated flow in porous media has an upper grain-size limit. For gravel-dominated sediments (> 2-mm grains), a much broader range of flow is determined by water films rather than by interconnected pathways of saturated pores. Studies are being conducted to determine how grain topography and water films control unsaturated flow in gravel.

A Hydrologic-Geophysical Method for Characterizing Flow and Transport. A University of Wisconsin/SNL project (70267) is using some of the techniques developed by another project (55332) to develop a hydrologic-geophysical method for characterizing flow and transport processes within the vadose zone. The method uses electrical conductivity information from electric resistivity tomography, dielectric constants obtained from cross-borehole ground-penetrating radar, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data to provide maps of hydrogeological heterogeneity and the extent of contamination. The objectives are to provide better models of flow and transport mechanisms within heterogeneous vadose zone deposits, a data base to assess the performance of the models, and a validated experimental method that could be applied to DOE sites to determine flow and transport rates.

Hydrogeology

Flow and Transport in Coarse Media. Some of the most badly contaminated DOE sites are at the Hanford site, where much of the vadose zone consists of coarse-textured materials with grain sizes greater than 1 millimeter. An LBNL project (70069) is designed to improve understanding of the flow and transport of contaminants in such sediments because some aspects of the flow in

coarse media are not predictable with classical modeling techniques. Their objectives are to quantify the macroscopic hydraulic properties of very coarse sediments and to determine the microscale basis for fast unsaturated flow. Macroscopic studies have used several different column methods. The microscopic tests of film flow have used the National Synchrotron Light Source at Brookhaven for the X-ray beam used to determine average water film thicknesses on Hanford gravel samples. The combined results of macroscopic and microscopic experiments will be used to develop a physical model of unsaturated flow in coarse sediments.

A Vadose Zone Observatory for Exploring Contaminant Transport. An LLNL project (70149), which is a continuation of a previous project (54950), is investigating details of contaminant transport in the vadose zone using the "Vadose Zone Observatory" at LLNL. The observatory has been designed to be particularly relevant for understanding contaminant transport issues at Hanford. The facility contains instrumented boreholes with electric resistance tomography arrays, wells for electromagnetic induction tomography, and tensiometers, lysimeters, and other sensors throughout the 70-foot zone between the surface and groundwater. Thus, infiltration events can be monitored using both geophysical imaging techniques as well as more conventional hydrologic measurements at discrete points. The infiltration studies involve releases of water at the surface, some with chemical tracers and some without added tracers for evaluating the effect of new infiltration on the downward movement of tracers remaining from previous releases. A computer modeling program is used to develop infiltration models for interpreting the wide variety of observations obtained during an infiltration experiment.

Project Teams

Lead Principal Investigator (Award Number)

- Lawrence Berkeley National Laboratory
  PI: Tetsu K. Tokunaga (70069)
- Lawrence Livermore National Laboratory
  PI: Patricia A. Berge (70108)
- Stanford University
  PI: Rosemary Knight (70115)
  University of British Columbia
- Lawrence Livermore National Laboratory
  PI: Charles R. Carrigan (70149)
- Pacific Northwest National Laboratory
  PI: Philip D. Meyer (70187)
- Pacific Northwest National Laboratory
  PI: Christopher J. Murray (70193)
  New Mexico Institute of Mining & Technology
- Sandia National Laboratories–Albuquerque
  PI: Gregory A Newman (70220)
  ElectroMagnetic Instruments, Inc.
- University of Wisconsin–Madison
  PI: David L. Alumbaugh (70267)
  Sandia National Laboratories–Albuquerque

Flow and Transport in Heterogeneous Porous Media. Accurate predictions of water flow and contaminant transport in the vadose zone are made more difficult because of the spatial variability of soils and sediments. This variability is difficult to characterize on a sufficiently small scale, so most models assume more uniform subsurface conditions than are actually present. A PNNL project (70187) is developing methods for combining small-scale direct measurements of soil physical and hydraulic properties with indirect geophysical measurements made at a larger scale to infer soil hydraulic properties at unsampled locations. These data are being used for model parameterization and numerical simulation of a large-scale, field injection experiment conducted at Hanford Site. The issue of parameter upscaling is being addressed as part of this research. The project is also investigating use of so-called pedo-transfer functions derived from neural network analyses to estimate model parameters. One of the key components of the research involves quantification of the prediction uncertainty associated with using sparse and/or surrogate data for model parameterization.

Role of Permeable, Vertical Structures in Contaminant Migration. Most flow and transport models of the vadose zone used in the past at the Hanford site assume horizontally layered sediments with no preferential vertical flow paths. But vertically oriented, more highly permeable structures occur at many locations in both the 200 West and 200 East areas, and these structures may enhance the vertical movement of moisture and contaminants through the vadose zone. A PNNL/New Mexico Institute of Mining and Technology project (70193) has involved a detailed ground-penetrating radar survey to identify the spacing and thickness of these vertical structures or clastic dikes. The distribution of hydraulic properties within clastic dikes is being measured using infiltration experiments. Geostatistical methods will then be used to provide numerical three-dimensional grids of the infiltration site for flow and transport modeling, and the resulting transport models will be compared with the actual observations.

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EMSP COLLABORATIONS

Research results are not always directly transferred to a specific end-user. Collaborations or interactions between EMSP researchers and others occur that increase the body of knowledge in a specific area as a direct result of EMSP funded research. This comes in many forms:

46 Consulting - provide advice or technical expertise
49 Joint interaction - researcher and end-user in joint interaction
19 Mission directed - project direction provided by end-user
60 Program interaction - researcher to researcher interaction

This section describes the reported collaborations that have occurred within the EMSP. Numerous other less formal collaborations occur during the EMSP topical and national workshops. Many of these are anticipated to mature into the research partnerships and research transfers reported elsewhere in this document.

DEACTIVATION AND DECOMMISSIONING

Analytical Chemistry & Instrumentation

Project: 65001

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

PI: Dr. Sanford A. Asher *Institution:* University of Pittsburgh

Description: When an analyte binds, its charge is immobilized within the acrylamide hydrogel. The resulting Donnan potential causes an osmotic diffracted wavelength shift and the color changes. The change in the wavelength diffracted reports on the identity and concentration of the target analyte. Our successful development of these simple, inexpensive highly-sensitive chemical sensing optrodes, which are easily coupled to simple optical instrumentation, could revolutionize environmental monitoring. In addition, we will develop highly rugged versions, which can be attached to core penetrometers and used to determine analytes, in buried core samples. Using this model, an on-going collaboration is occurring with the Nevada Field Office to address their need for uranium detection in soils and groundwater.

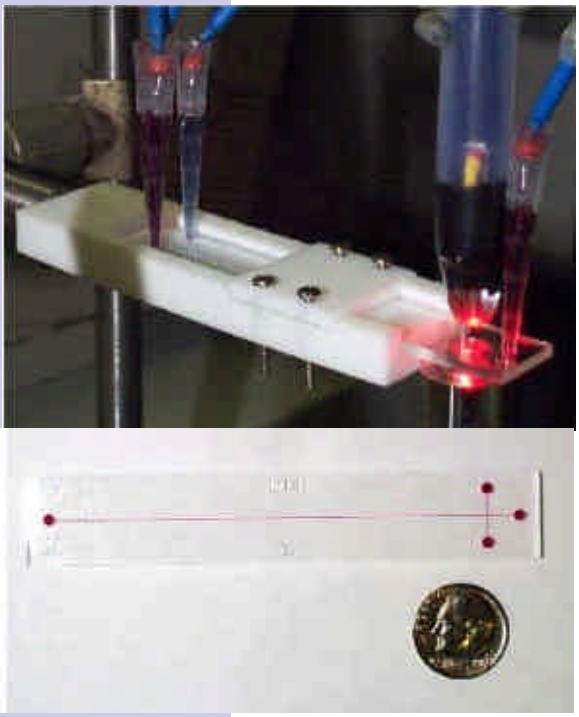
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: John Jones and Bruce Crow
Collaborating Organization: DOE-NV

Project: 82749 (Renewal of Project 64982)

Title: Field Portable Microchip Analyzer for Airborne and Surface Toxic Metal Contaminants

PI: Dr. Greg E. Collins *Institution:* Naval Research Laboratory

Description: This project addresses the need for developing a new class of radionuclide and heavy metal complexation agents that are tagged with near-infrared dyes and can therefore be extended to the implementation of a compact and portable "laboratory-on-a-chip" operable in the stringent field requirements of DOE site characterization and remediation. As such, this project is also working directly with the Nevada Field Office to address their need for uranium detection in soils and groundwater.



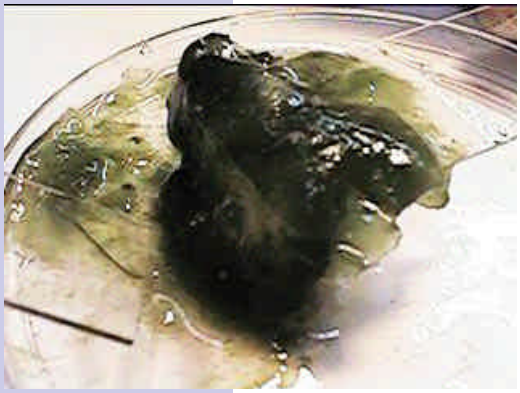
The portable Lab-on-a-Chip Sensor for Radionuclide and Heavy Metals is intended to provide a field portable characterization instrument for in-situ waste characterization. [see Project #82749, renewal of #64982]

Collaboration Type: Joint interaction
Fiscal Year: 2001
Collaborator: John Jones and Bruce Crow
Collaborating Organization: DOE-NV

Description: This project addresses the need for developing a highly sensitive and selective portable radionuclide analyzer which would permit a low-cost and timely characterization of DOE remediation sites. Through the application of near-infrared fluorophore tagged macrocycles, in combination with the capillary electrophoretic separation of radionuclide and heavy metal complexes on a microchip, we propose an innovative, low cost characterization approach to gaining timely characterization data in the field. DDFA has committed to perform Large Scale Demonstration on the "Laboratory-on-a-Chip."

Collaboration Type: Joint interaction
Fiscal Year: 1999
Collaborator: Dick Meservey
Collaborating Organization: INEEL

Biogeochemistry



The abundant synthesis of biopolymers by algae (*Nostoc* sp. GSV40). [see Project #64907]

Project: 64907

Title: "Green" Biopolymers for Improved Decontamination of Metals from Surfaces: Sorptive Characterization and Costing Properties
PI: Dr. Brian H. Davison
Institution: ORNL

Description: Entered discussions with algal biomass producers at Hebrew University and Ben Gurion University, both of Israel, on selection and production of biopolymer. Inexpensive production of the biopolymers is essential for the ultimate application. We established contacts with several researchers and developers in growing algae in

bulk. These include commercial demos of biosorption in the U.S. Collaborations in detail will need to wait for selection of a biopolymer and completion of preliminary proof-of-concept tests.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Elisha Ter-Or and Shosham Arad
Collaborating Organization: Hebrew University and Ben Gurion University

Engineering Science

Project: 55052

Title: Advanced Sensing and Control Techniques to Facilitate Semi-Autonomous Decommissioning
PI: Dr. Robert J. Schalkoff *Institution:* Clemson University

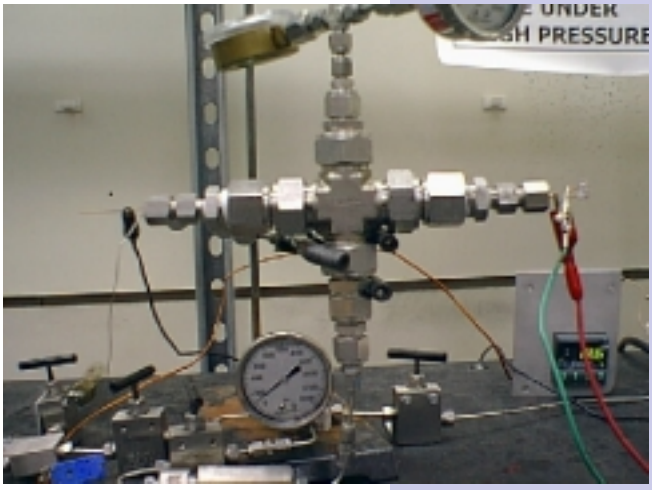
Description: The researchers for this project identified an end-user and began collaborations with the INEEL Decontamination, Decommissioning, and Remediation Optimal Planning System (DDROPS). The INEEL system has widespread applicability throughout DOE and is leading edge technology estimated to save the DOE millions of dollars. The goal is to incorporate EMSP's near real-time virtual reality modeling and imaging system as a component of the larger INEEL system.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dick Meservey
Collaborating Organization: INEEL

Project: 64979

Title: Basic Engineering Research for D&D of R.Reactor Storage Pond Sludge: Electrokinetics, Carbon Dioxide Extraction, and Supercritical Water Oxidation
PI: Dr. Edward A. Hamilton *Institution:* SCUREF

Description: Large quantities of mixed low level waste (MLLW) that fall under the Toxic Substances Control Act (TSCA) exist and continue to be generated at DOE sites across the country. Currently, the volume of these wastes is 23,500 m3, and the majority of these wastes (i.e., almost 19,000 m3) consists of PCBs and PCB-contaminated materials. Although a number of processes have been proposed for the recovery and/or destruction of these persistent pollutants, none has yet to emerge as the preferred choice for DOE cleanup. Recently, researchers at the INEEL indicated the possibility of previous DOE projects examining the use of SCWO to destroy chlorinated organics as a potential starting point for this project. Karen Moore of the INEEL will send a detailed list of literature references from the final project report on SWCO along with a copy of the final project report.



Electrochemical Cell at the University of South Carolina [see Project #64979]

Collaboration Type: Program interaction
Fiscal Year: 2000
Collaborator: John Beller and Karen Moore
Collaborating Organization: INEEL

Description: Collaborating researchers at the University of South Carolina (USC), Clemson University (CU), and the SRS (SRS) are investigating the fundamentals of a combined extraction and destruction process for the decontamination and decommissioning (D&D) of PCB-contaminated materials as found at DOE sites. Currently, the volume of PCBs and PCB-contaminated wastes at DOE sites nationwide is approximately 19,000 m3. While there are a number of existing and proposed processes for the recovery and/or destruction of these persistent pollutants, none has emerged as the preferred choice. Therefore, this research focuses on combining novel processes to solve the problem. The research objectives are to investigate benign dense-fluid extraction with either carbon dioxide (USC) or hot water (CU), followed by destruction of the extracted PCBs via either electrochemical (USC) or hydrothermal (CU) oxidation. Based on the results of these investigations, a combined extraction and destruction process that incorporates the most successful elements of the various processes will be recommended for application to contaminated DOE sites.

The SCUREF Project Director coordinates the activities of the three components of the research team, reviews bi-monthly progress reports, and conducts quarterly team meetings to share research results. The SRS component of the Project Team provides regulatory compliance information regarding PCB handling and usage, and provides model matrix material. This model material, used in the field to absorb PCB-contaminated liquids, will be contaminated in the lab and used for extraction experiments. The Savannah River Technology Center (SRTC) investigator will analyze matrix material that has been processed by SCUREF investigators for effectiveness of the extraction and destruction processes. In year three of the project, graduate students will spend a portion of the year on site performing experiments with PCBs under the supervision of the SRS team members. Also in year three, SRTC, using laboratory results provided by SCUREF investigators, will develop conceptual process designs for decontamination of PCB-contaminated matrices. The SRTC PI will evaluate these designs for technical and economic feasibility.

Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborator: Mike Matthews, David Bruce, Mark Thies, Lawrence Oji, John Pickett, Nancy Lowry
Collaborating Organization: Clemson University; University of South Carolina; Savannah River Technology Center; Facilities Decommissioning Division, WSRC.

Description: The INEEL has provided a detailed spreadsheet of all their PCB mixed wastestreams to provide the researchers a understanding of the maginitude of the problem. The INEEL also has offered to put the researcher in contact with wastestream owners if more information is required.

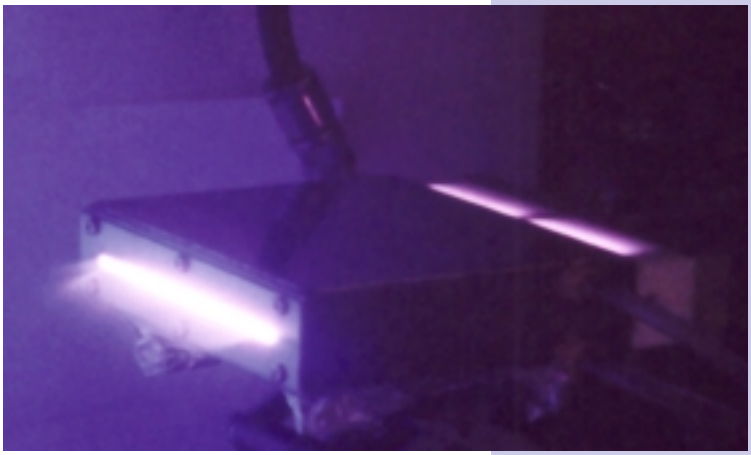
Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Mark Argyle
Collaborating Organization: INEEL

Materials Science

Project: 73835 (Renewal of Project 54914)

Title: Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces
PI: Dr. Robert F. Hicks *Institution:* University of California at Los Angeles

Description: The researchers for this project have initiated collaborations with the INEEL and LANL and are directing their research towards specific needs at these end-user sites. The INEEL has provided the Atmospheric-Pressure Plasma Jet (APPJ) project with coupons coated with surrogate contamination allowing the researchers to evaluate the work in laboratory conditions. This project has wide spread application at all DOE sites with TRU contaminated buildings, equipment, or wastes. The goal of this technology is to remove TRU-contamination, allowing the contaminated waste to be treated as clean waste or to be re-classified to a lower level. This science is a dry application that generates very little secondary waste making it very appealing to any baseline processes.



Front view of a 4" wide thermospheric-pressure plasma source operating with 750 Torr helium and 10 Torr oxygen. [see Project #73835, renewal of #54914]

Collaboration Type: Mission directed *Fiscal Year:* 2001
Collaborating Organization: INEEL and LANL

Separations Chemistry

Project: 60283

Title: Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation
PI: Dr. Michael J. Pellin *Institution:* ANL

Description: The waste stream generated in the D&D efforts for nuclear facilities includes a significant volume of material that is contaminated only in the surface or near-surface region. It is critical to understand the depth-dependent concentration and chemistry of radionuclide-contaminated surfaces. Complete removal and capture of the contaminated surface would greatly reduce the volume of waste material generated in, and thus the cost of, D&D efforts. This project represents the first detailed surface

studies of the sorption of radionuclides in complex materials such as concrete. Collaboration is a joint interaction with Zawtech Inc. to do further research into areas of practical applications in industry.

Collaboration Type: Joint interaction *Fiscal Year:* 1999
Collaborating Organization: Zawtech Inc.

Project: 64912

Title: Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners
PI: Dr. David W. DePaoli *Institution:* ORNL

Description: This project is focused on surface decontamination using environmentally benign aqueous cleaners, specifically the removal of organic contaminants using surfactant solutions. Facilities throughout DOE have need for removal of organics (oils, PCBs, etc.) from solid substrates, particularly metals surfaces such as ductwork, pumps, tools, gloveboxes, etc. Aqueous-based solutions are attractive alternatives to chlorinated/fluorinated solvents that have been banned or are being phased out. They promise several advantages for decontamination processes, including low hazard potential, low cost, and reduced secondary waste volume. Laboratory-scale experimentation has been aimed at determining improved means for removal of organic contaminants using aqueous surfactant cleaners. We have found that the rate of oil removal can be significantly increased through a simple modification of process conditions. An invention based on our findings has been communicated, through a non-disclosure agreement, with a leading company that produces industrial cleaners. That company has agreed to collaboratively participate in testing of the technology through guidance and evaluation. Company representatives have arranged a visit to ORNL and the University of Tennessee on September 28, 2000 to evaluate the potential of the technology and to discuss partnership and commercialization.

Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: ORNL/ University of Tennessee

Description: Work is currently being done with Dick Meservey and Amy Mikkola of the "New Idaho Large-scale Decontamination and Decommissioning Project" at the Idaho Engineering and Environmental Laboratory to identify specific site applications, perform bench-scale testing, and evaluate feasibility for incorporation into large-scale demos. The understanding developed in this work will be directly applied to decontamination/decommission tasks by testing surface samples from DOE contaminated sites (such as those from the enrichment process building of K-25 site) and will provide the basis for improved approaches for removal of organic contamination by synthetic surfactants. These improvements will lead to decreased hazards for workers, decreased secondary waste generation, increased efficiency, and lower cost. The proposed research program is a multi-disciplinary and multi-*Institution*al collaboration between a national laboratory and a university. The team includes engineers and scientists with expertise in colloid and interfacial phenomena and separation processes.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dick Meservey and Any Mikkola
Collaborating Organization: INEEL

Description: We have an alliance with Petroferm Inc. of Fernandina Beach, Florida (A leader in industrial oil/grease removal technology) and are at the point of demonstrating our advanced technologies; our primary contact there is Dr. Nelson E Prietro (Technical Director). Petroferm is very interested in the general industrial applications in addition to D&D applications. We are currently involved with discussions on commercialization of the technology as well as additional laboratory and theoretical exploration. Current technology is focused on metal components that may be submerged in water-filled tanks. His use for the current technology is slightly different that we envisioned at the beginning of our research.
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dr. Nelson E Prietro
Collaborating Organization: Petroferm Inc.

HEALTH/ECOLOGY/RISK

Health/Risk

Project: 54546

Title: Engineered Antibodies for Monitoring of Polynuclear Aromatic Hydrocarbons
PI: Dr. Alexander E. Karu *Institution:* University of California at Berkeley

Description: The objective of this project is to use molecular biological techniques to derive a set of antibodies with useful affinities and selectivities for recovery and detection of polynuclear aromatic hydrocarbons (PAHs) in environmental and biological samples. The long-term goal is to develop immunodetection methods that will be useful in biomarker research and regulatory monitoring of PAHs. This project has established a collaboration with Dr. Tuan Vo-Dinh at ORNL to identify a sensor system and perform a demonstration.
Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborator: Dr. Tuan Vo-Dinh
Collaborating Organization: ORNL

Project: 54684

Title: Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup
PI: Dr. Brian D. Thrall *Institution:* PNNL

Description: EPA is using the data we have generated and a paper describing the mode of action for induction of liver tumors to revise their risk assessment on trichloroethylene. EPA continues to track our published results as this decision process reaches its conclusions. A separate step will be actions taken under the Office of Water to revise drinking water standards or CERCLA to modify clean-up standards that are derived from the revised risk assessments.

Collaboration Type: Consulting *Fiscal Year:* 1998
Collaborating Organization: EPA

Project: 55410

Title: Determining Significant Endpoints for Ecological Risk Analysis
PI: Dr. Thomas G. Hinton *Institution:* Savannah River Ecology Laboratory

Description: Protection of the environment from ionizing radiation, and the associated questions we are addressing through the EMSP program, are of national and international interest. We were asked to present our results and provide guidance at two important meetings. Nationally, the DOE is formulating guidance on how to conduct ecological risk anlayses through their Biota Dose Assessment Committee. Dr. Hinton asked to review their documents, and present our research results at a meeting in Aug. 1999. At the international level, Dr. Hinton was asked to be on a panel of experts at an International Atomic Energy Agency meeting in Vienna, Austria (Aug. 2000).

We addressed the issue of what are the appropriate endpoints when conducting ecological risk analyses, and whether or not the environment is automatically protected when exposures are limited to the point that humans are protected.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborating Organization: International Atomic Energy Agency

Description: Our interest is in obtaining a scientifically defensible endpoint for measuring ecological risks to populations exposed to chronic, low-level radiation, and radiation with concomitant exposure to chemicals. To do so, we believe that we must understand the extent to which molecular damage is detrimental at the individual and population levels of biological organization. Ecological risk analyses based on molecular damage, without an understanding of the impacts to higher levels of biological organization, could cause cleanup strategies on DOE sites to be overly conservative and unnecessarily expensive. The PI has taken knowledge gained from this research and used it in his work with the DOE Biota Dose Assessment Group (BDAG). BDAG is currently reviewing ecological risk concepts and establishing guidelines for conducting ecological risks on DOE Facilities.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Thomas Hinton
Collaborating Organization: Savannah River Ecology Lab - University of Georgia

Project: 60037

Title: Estimation of Potential Population Level Effects of Contaminants on Wildlife
PI: Dr. James Loar *Institution:* ORNL

Description: Although risk managers for CERCLA sites are concerned with risks to wildlife populations, methods for wildlife risk assessments are based on

effects on individuals. The purpose of this project is to provide DOE with methods to assess risks to wildlife populations. In support of program objectives, a series of conference call meetings were held with these individuals to utilize their expertise in various areas.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: John D. Eisemann/ Rick Bennett/ Pierre Mineau/ Bruce Hope/ Clarence Callahan & Ned Black/ Regina Donahoe/ Jim Polinski/ Nathan Schumaker
Collaborating Organization: Nat. Wldlf. Res. Ctr. (USDA APHIS); Wldlf. Toxic., EPA Dul. Lab.; Can. Wldlf. Serv.; Ecorisk, Oregon Dept. of Env. Qual.; CA state regs.; EPA Reg. 9; CA. Off. Env. Health Haz. Ass.; CA Dept. of Toxic Subs. Control; and EPA, Corvallis, OR.

Project: 73942 (Renewal of Project 59918)

Title: Improved Radiation Dosimetry Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites
PI: Dr. Bobby R. Scott *Institution:* Lovelace Biomedical & Environmental Research Institute

Description: Additional data on lung cancer induced in Mayak workers exposed by inhalation to both plutonium and cigarette smoke were acquired by Dr. Scott from scientists at the Branch No. 1 of the Institute of Biophysics, Ozersk Russia. The data will facilitate making conclusions about possible interactions between alpha radiation and cigarette smoke in the induction of lung cancer. The data will also allow for additional insights to be made related to the validity of the linear, no-threshold hypothesis for cancer induction.

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborator: Unknown
Collaborating Organization: Branch No. 1 of the Institute of Biophysics, Ozersk Russia

Description: We are now assisting staff at the Rocky Mountain Remediation Services, L.L.C., Rocky Flats Environmental Technology Site in preparing a scientifically valid approach to selecting respiratory protection devices for use in very high concentrations of plutonium. Some concentration of interest would essentially lead to early occurring or delayed deaths without adequate worker protection. The activities at Rock Flats relate to decontamination and decommissioning. Our staff reviewed an original draft white paper related to selecting appropriate respiratory devices and major shortcomings related to protecting DOE decontamination/decommissioning workers were pointed out. We will continue to assist in preparing a more credible plan for protecting workers and in preparing an associated white paper.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Rocky Mountain Remediation Services, L.L.C.,
Collaborating Organization: Rocky Flats Environmental Technology Site

Description: The Department of Energy has standards that require evaluating non-cancer-producing radiological doses to the immediate worker in order to know the intake level that corresponds to serious injury or prompt death. Historically, only criticality prompt doses have been calculated and characterized as high, moderate, or low. Doses associated with inhalation intakes have not been adequately evaluated. Rather, they have only been subjectively indicated as high, moderate, or low, with little scientific justification. Rocky Flats Environmental Technology Site (RFETS) scientists are faced with evaluating intakes of plutonium aerosols that would be associated with serious radiation deterministic effects (e.g., respiratory dysfunction, death from radiation pneumonitis), following a plutonium (Pu) accident involving inhalation exposure. Such accidents could arise during decommissioning/deactivation operations related to Pu-contaminated facilities. Researchers have assisted RFETS scientists in evaluating risks to RFETS workers for radiation-induced deterministic effects in the lung associated with accident scenarios related to inhaling mixtures of Pu-238, Pu-239, Pu-240, Pu-241, and Am-241. These mixtures arise for weapons-grade Pu, aged weapons-grade Pu, and high Am-241 residue that contains Pu. The normalized-dose risk model developed by Dr. B. R. Scott for radiation-induced deterministic effects was used. Variability and uncertainty were accounted for via the use of distributions for model parameters previously published by Dr. Scott. Results indicate that milligram quantities of mixtures involving the indicated isotopes must be inhaled in order to produce deterministic effects in the lung. The cited intake includes inhaled material that is not deposited in the respiratory tract. However, rather than occurring promptly, the deterministic effects may occur months to years after inhaling the Pu/Am, as threshold radiation dose for deterministic effects may not be reached until such times after inhalation exposure.

Collaboration Type: Consulting *Fiscal Year:* 2001
Collaborator: Dr. Vern L. Peterson
Collaborating Organization: Rocky Flats Environmental Technology Site

Description: For years, there has been concern about possible harm to the general public from plutonium (Pu) contamination at the U.S. Department of Energy's Rocky Flats Environmental Technology Site. Until recently, little information was available on Pu risks based on actual human exposure to Pu isotopes. Lung cancer risks estimates for humans that inhale Pu therefore are based largely on extrapolations from animal studies or extrapolations from experience with external radiations (e.g., atomic bomb survivors) or on persons exposed to radon. Now it is known that the radiation dose from radon is spread differently over the lung than is the case for Pu aerosols; thus, risks estimates based on radon are inappropriate for Pu aerosols. With partial support from EMSP Project 59918, a joint Russian/U.S. case-control study of lung cancer induction by inhaled Pu-239 plus gamma rays, as well as cigarette smoke, has been conducted, which provides new insights about pair-wise interactions of the indicated three factors in lung cancer induction. Dr. Z. B. Tokarskaya of the First Institute of Biophysics, Ozersk Russia, headed the study. The database used relates to Mayak plutonium production

facility workers in the Chelyabinsk region of Russia. The study included 486 individuals (162 cases), with matching of 2 controls per case. Three levels of smoking were considered: low (controls), middle, and high. Using odds-ratio methods to investigate pair-wise interactions, synergistic interactions were demonstrated for radiation (gamma dose or Pu-239 body burden) plus high levels of smoking. Otherwise additive effects could not be ruled out for smoking and radiation. However, combined exposure to external gamma rays and Pu-239 caused a dramatic synergistic interaction, which is consistent with threshold-type risk vs. dose relationships for radiation. Although these results are preliminary, demonstration of a threshold for Pu-induced lung cancer could significantly alter cleanup criteria for Pu-contaminated sites such as Rocky Flats.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. Z. B. Tokarskaya
Collaborating Organization: First Institute of Biophysics (FIB-1) Ozersk, Russia

Project: 74050 (Renewal of Project 59882)

Title: Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at US DOE Fernald
PI: Dr. Naomi H. Harley *Institution:* New York University Medical School

Description: One objective of this project is to develop the sequential radiochemistry necessary to measure any environmental sample for the isotopes of uranium, thorium, radium, and lead-210. To utilize this radiochemistry for lead-210 before and after the radium is removed form the silos to accurately determine the amount of radon gas released, from the parent radium during removal. To utilize the radiochemistry to accurately trace and delineate thorium, radium, and uranium nuclides, originating from Fernald, in the environment. Dr. Fisenne at DOE Environmental Measurements Laboratory has developed a sequential radiochemical procedure to analyze any environmental sample matrix, presently focused on Soil samples, for Lead-210, radium, thorium, and uranium isotopes. We are currently cunsulting with Dr. Fisenne.

The insides of the radon-222, radon-220 monitor device. [see Project #74050, renewal of #59882]

Collaboration Type: Consulting
Fiscal Year: 1999
Collaborator: Dr. Isabel Fisenne
Collaborating Organization: Environmental Measurements Laboratory

Low Dose Radiation

Project: 69904

Title: Low-Dose Risk, Decisions, and Risk Communication
PI: Dr. James Flynn *Institution:* Decision Science Research Institute

Description: Science and Risk at the Community Level: Three Case Studies - A social research project on science and risk information roles in guiding the attitudes, opinions, perceptions and preferences of community-level residents. In a joint effort we have conducted preliminary examination of 14 potential communities located near DOE and nuclear power generating facilities. Three communities have been chosen for in-depth studies. Fieldwork in these three communities is now underway.
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: S. Tuler, T. Webler, and J. Wilhoit
Collaborating Organization: Decision Research and the Social and Environmental Research Institute

Description: Decision Research sponsored a three-day workshop held in Eugene, Oregon, June 12-14, 2000. The event brought together twenty researchers from 10 *Institution*s to examine the role of science and risk communication in presenting the results of the DOE Low Dose Radiation Research Program. A transcript of the Workshop proceedings is posted at the Decision Research web site: www.decisionresearch.org.
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: A. Brooks, R. Kasperson, S. Tuler, W. Freudenburg, S. Friedman, B. Wynne, J. Kasperson, N. Pidgeon, E. Omohundro, D. Lash, S. Johnson
Collaborating Organization: Washington State University; Clark University; The Social and Environmental Research Institute; University of Wisconsin, Madison; Lehigh University; Lancaster University (UK); Oregon State University; University of East Anglia (UK); University of Oregon

Project: 69906

Title: Markers of the Low-Dose Radiation Response
PI: Dr. William S. Dynan *Institution:* Medical College of Georgia

Description: Researchers on this project are seeking to identify subtle changes in living cells that occur in response to low-level radiation exposure. A new approach has recently been initiated to perform a comprehensive survey of radiation-induced changes in the cellular protein complement. The work uses a novel 2D-differential in-gel electrophoresis technology supplied as part of a partnership between the Georgia Research Alliance, University of Georgia System, and Amersham Pharmacia Biotechnology. Extracts are prepared from treated and untreated (control) cells, labeled with differently colored dyes, mixed, and subjected to co-electrophoresis in a two-dimensional gel system. Gels are then scanned and fluorescence in each color

range is compared. Specialized software identifies protein spots that increase or decrease upon treatment. Spots are then robotically excised and identified by mass spectrometry.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborating Organization: Georgia Research Alliance, University of Georgia System, Amersham Pharmacia Biotechnology, University of Maryland

Description: We seek to develop a technology that will allow direct visualization of DNA double-strand break repair complexes in their original places in the nuclei of irradiated cells. These studies will help bridge the gap between biochemical studies of repair enzymes and an understanding of the process of repair as it actually occurs within the radiation-injured cell. We have made new plans to collaborate with Dr. Thomas Orlando, who is developing a new type of inexpensive micro-irradiation probe. We will irradiate single cells and study the effect on our markers both in the target cells and in bystander cells.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dr. Thomas Orlando
Collaborating Organization: Georgia Institute of Technology

HIGH-LEVEL WASTE

Actinide (Heavy Element) Chemistry

Project: 65398

Title: Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leach Solutions
PI: Dr. Kenneth L. Nash *Institution:* ANL

Description: Our project investigating the chemistry of actinides in strongly alkaline media continues to make progress on understanding the behavior of actinides in alkaline solutions and sludge simulants. We were recently contacted by the SRS inquiring after our observations regarding the behavior of uranium during the washing of PUREX sludge simulants in connection with some work they are involved in regarding waste tank remediation. SRS has some solid material that may contain moderate concentrations of enriched uranium. Their concern is to make certain that they won't accidentally assemble a critical mass during this dissolution procedure. Their inquiry specifically targeted the solubility limits for uranium in alkaline solutions, which we indicated based on the results of our EMSP project to be in the range of 1-2 x 10-5 M, in general agreement with literature predictions (based on information obtained under somewhat different conditions). Our observations essentially confirmed their expectations.

Collaboration Type: Consulting *Fiscal Year:* 2001
Collaborator: David Hobbs
Collaborating Organization: SRS

Project: 73759 (Renewal of Project 54679)

Title: Computational Design of Metal Ion Sequestering Agents

PI: Dr. Benjamin P. Hay *Institution:* PNNL

Description: Critical tasks in the cleanup of U.S. Department of Energy (DOE) sites include processing radioactive wastes for disposal in long-term storage, remediation/restoration of environmental sites resulting from radioactive contamination, and decontamination/decommissioning of nuclear facilities. Because the radioactive components, most of which are metals, are typically present in very low concentrations, it is desirable to remove them from the bulk of the contaminated source and concentrate them to minimize the volume of radioactive material destined for permanent subsurface disposal and thus minimize disposal costs. Over the past 50 years, much research has focused on the discovery of selective ligands for f-block metal separations; both neutral and ionic ligands have been examined. Despite past success in the discovery of ligands that exhibit some degree of specificity for the f-block metal ions, the ability to further control binding affinity and selectivity remains a significant challenge. The objective of this project is to provide the means to optimize ligand architecture for f-block metal recognition. Criteria for accurately selecting target ligands would result in a much more effective use of resources, thereby reducing the time and cost associated with metal-specific ligand development. Collaborations for each associated task are as follows:

Task: Synthesis and characterization of modified calixarene host molecules.

- Professor D. Max Roundhill, Department of Chemistry, Texas Tech University

Task: Crystal structure determinations.

- Professor Robin D. Rogers, Department of Chemistry, The University of Alabama

Task: Synthesis of amides and diamides, through a subcontract with Associated Western Universities to support a Postdoctoral Fellow, Dr. Robert Gilbertson, in Dr. Hutchison's group.

- Professor James E. Hutchison, Department of Chemistry, University of Oregon

Task: Provide structure-function data on catecholates and hydroxypyridonates.

- Professor Kenneth N. Raymond, Department of Chemistry, University of California at Berkeley

Task: Provide structure-function data on pyridine N-oxides.

- Professor Robert T. Paine, Department of Chemistry, University of New Mexico

In addition to interactions with University faculty, the project has supported a variety of visitors at PNNL through Associated Western Universities subcontracts, including:

- Dr. Pier L. Zanonato (Visiting Faculty, University of Padova, Italy) - calorimetry
- Dr. Bruce K. McNamara (Postdoctoral Fellow) - calorimetry, spectroscopy, solvent extraction
- Dr. Omoshile Clement (Postdoctoral Fellow) - molecular mechanics
- Dr. Giovanni Sandrone (Postdoctoral Fellow) - quantum mechanics
- Dr. Rubicelia Vargas (Post Doctoral Fellow) - molecular mechanics and quantum mechanics
- Dr. Jorge Garza (Visiting Faculty, Metropolitan Autonomous University -Iztapalapa, Mexico) - quantum mechanics

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Heavy Metals was started by this group in September 1997
Collaborating Organization: (See description)

Project: 81887 (Renewal of Project 65411)

Title: Precipitation and Deposition of Aluminum-Containing Phases on Tank Wastes
PI: Dr. Shas Mattigod *Institution:* PNNL

Description: Aluminum-containing phases represent the most prevalent solids that can appear or disappear during the processing of radioactive tank wastes. Of all constituents of tank waste, Al-species have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and completely shutting down processing operations. The primary focus of this project is to understand the major factors controlling precipitation, scale formation, and cementation of existing soluble particles by Al-containing phases. The results will be used to predict and control precipitation, scale formation, and cementation under tank waste processing conditions. The results will also provide information regarding what Al-containing phases form and how soluble such phases are in basic tank waste solutions. The project will have an important impact on waste minimization and on the retrieval, transport, and separation of tank wastes. Collaboration with Dr. Albert Hu at Lockheed Martin Hanford Company to perform simulations to support the ESP modeling work at Hanford.

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: Dr. Albert Hu
Collaborating Organization: Lockheed Martin Hanford Company

Analytical Chemistry & Instrumentation

Project: 55318

Title: Improved Analytical Characterization of Solid Waste Forms by Fundamental Development of Laser Ablation Technology
PI: Dr. Richard E. Russo *Institution:* LBNL

Description: Characterization continues to be a need within the DOE EM program in the areas of high-level waste, tanks, sub-surface contaminant plumes, D&D activities, spent nuclear fuel, mixed wastes, and plutonium disposi-

tion. Laser ablation can provide direct characterization of any solid waste form in a timely manner and at a reduced cost compared to conventional analytical dissolution procedures. The primary technical difficulties hindering this technology are matrix dependence and fractionation, both effect accuracy of quantitative characterization. These issues must be understood on a fundamental level to develop laser ablation as a routine characterization technology. Understanding these fundamental issues is the basis of the EMSP project. The PI has established an interaction with the primary personnel responsible for setting up the laser ablation inductively coupled plasma - mass spectroscopy (LA-ICP-MS) system in Building 222S at PNNL. The PI has visited the Hanford Site and toured the LA facility.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: John Hartman, Mike Alexander, and Monte Smith
Collaborating Organization: PNNL

Description: DOE Materials Disposition Program is developing two LA systems, at SRS and LLNL for Pu characterization. Because of the reputation of the PI and the EMSP program, Russo was asked to help develop the systems and standards for this PuO2 effort.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: Chris Bannochie
Collaborating Organization: DOE Savannah River

Description: This project has continuing interaction with other EMSP investigator studying laser ablation. This includes projects 55205 - A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals, and 60283 - Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Dr. Scott Goode and Dr. Michael J. Pellin
Collaborating Organization: University of South Carolina and ANL

Project: 60075

Title: Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations
PI: Dr. J. Thomas Dickinson *Institution:* Washington State University

Description: Methods for compositional analysis of fissile materials and radioactive/ toxic wastes are being developed to support characterization prior to treatment and remediation. The need for rapid, real-time, on-site characterization of waste at DOE sites has led to deployment of laser ablation-inductively coupled plasma mass spectroscopy (LA/ICP-MS) systems for elemental and isotopic analysis at several locations, including Hanford, Los Alamos, and the INEEL. These systems can provide qualitative or semi-quantitative analysis of certain sample types with minimal sample handling. Research into the fundamental physical processes of particle formation

during laser ablation is required to provide basic understanding that will allow us to maximize the utility of these systems. As such, an on-going collaboration is occurring with the Nevada Field Office to address their need for uranium detection in soils and groundwater.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: John Jones and Bruce Crow
Collaborating Organization: DOE-NV

Description: We have been working with Dr. Beverly Crawford. Dr. Crawford is in charge of a laser ablation ICP-MS system that has been installed in a hot cell in the Hanford 222S building. One of the key technical questions is how well laser ablation can determine the overall bulk composition of a heterogeneous sample given a small volume of material sampled. We have begun to address the homogeneity issue.

Collaboration Type: Joint interaction *Fiscal Year:* 1999
Collaborator: Jim Rindfleisch
Collaborating Organization: Long Range Waste Management Program, INEEL

Description: Performing laser ablation/description analytical determination on a surrogate sample. Contacted Arlin Olson and Scott Herbst to identify the surrogate and analytical requirements. Investigate analysis of these samples by laser ablation IMP-MS as well as a related method, laser desorption mass spectroscopy to determine key molecular components. The goal is to generate a complete mass balance of the calcine waste.

Collaboration Type: Joint interaction *Fiscal Year:* 1999
Collaborator: Dr. Beverly Crawford
Collaborating Organization: Numatec, Hanford

Project: 60219

Title: Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste
PI: Dr. Digby D. MacDonald *Institution:* Pennsylvania State University

Description: The principal goals of this project are to develop advanced electrochemical emission spectroscopic (EES) methods for monitoring the corrosion of carbon steel in simulated DOE liquid waste and to develop a better understanding of the mechanisms of the corrosion of metals and alloys in these environments. To faciliate this goal, interaction with SRI International has been begun.

Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborator: Dr. George Engelhardt
Collaborating Organization: SRI International

Engineering Science

Project: 54656

Title: Mixing Processes in High-Level Waste Tanks
PI: Dr. Per F. Peterson *Institution:* University of California at Berkeley

Description: Flammable gases can be generated in DOE high-level waste tanks. This project is a concentrated effort to develop models and a numerical tool to mechanistically predict mixing processes in large waste-tank volumes, where mixing processes can be driven by hot and cold vertical and horizontal surfaces and injected buoyant jets. General Electric is funding a doctoral student to work on this project.

Collaboration Type: Consulting *Fiscal Year:* 1999

Collaborating Organization: General Electric

Project: 60143

Title: Foaming in Radioactive Waste Treatment and Immobilization Processes

PI: Dr. Darsh T. Wasan *Institution:* Illinois Institute of Technology

Description: The physical mechanisms of the formation of foam in radioactive waste treatment and waste immobilization processes are poorly understood. The objective of this research is to develop a basic understanding of the mechanisms that produce foaming, to identify the key parameters which aggravate foaming, and to identify effective ways to eliminate or mitigate foaming. We are working with Savannah River Salt Processing Project to help evaluate and select optimal foaming agent to mitigate foaming problems that occurred in the Small Tank Tetraphenylborate Precipitation (STTP) program.

Collaboration Type: Consulting *Fiscal Year:* 2001

Collaborating Organization: Savannah River Salt Processing Project and Tanks Focus Area

Description: Illinois Institute of Technology (IIT) has been working closely with the Savannah River Technology Center in the development of an improved antifoaming agent for the Defense Waste Processing Facility (DWPF). The key to the development of this new antifoam agent was a close working relationship between the IIT researchers and the customer (Dan Lambert) at the SRS (SRS). University and national lab researchers often come up with unique and innovative solutions that are useless to the customer. The reason for the success of this project can be attributed to the fact that the IIT researchers sought to understand the science and the limitations in the customer's waste processing facility through close working relationships.

Collaboration Type: Mission directed *Fiscal Year:* 2000

Collaborating Organization: Savannah River Technology Center

Project: 81897 (Renewal of Project 65435)

Title: Millimeter-Wave Measurements of High Level and Low Activity Glass Melts

PI: Dr. Paul P. Woskov

Institution: Massachusetts Institute of Technology

Description: Laboratory experiments at MIT have established the feasibility for real-time monitoring of all thee parameters, temperature, conductivity, and viscosity. Also a new capability for molten glass density measurements at

high-temperature was discovered. A key milestone in the second year was a meeting with Tank Focus Area representatives at MIT on December 7, 1999, to discuss monitoring priorities and the transfer of this technology to TFA.

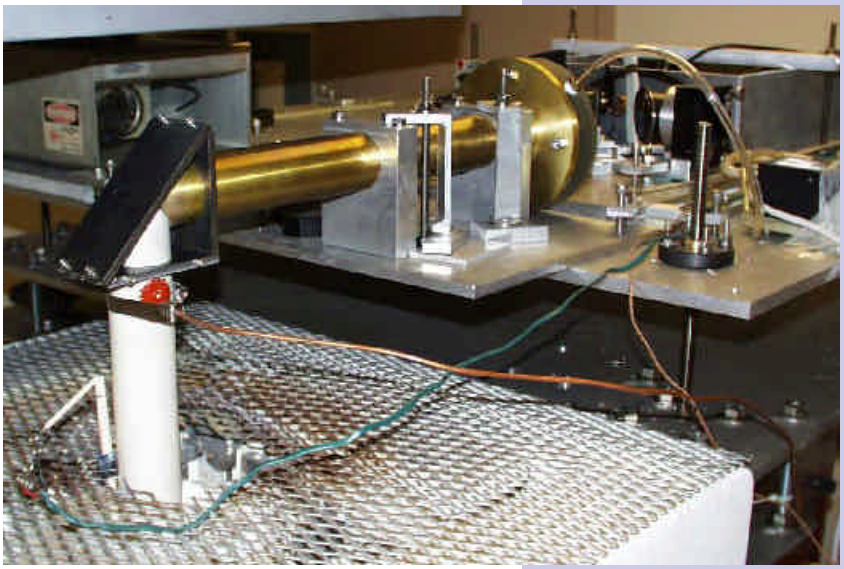
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Bill Holtzcheiter, Frank Thomas III, from SRTC; Tom Thomas, from INEEL; Glenn Bastiaans, from Ames; S. K.. Sundaram, from PNNL
Collaborating Organization: Tanks Focus Area

Description: The developments of this project are being closely monitored by the Tank Focus Area (TFA). A formal meeting with TFA representatives was held at Plasma Science Fusion Center, Massachusetts Institute of Technology on December 7, 1999 to discuss the transfer of the millimeter-wave-based melter diagnostics technology being developed under the EMSP project (PNNL-MIT-SRTC). The meeting was successful in identifying potential deployment of millimeter wave technology to meet the needs of the TFA. The participants of the meeting were as follows:

- PNNL - S. K. Sundaram
- MIT - Paul Woskov, Paul Thomas, Kamal Hadiddi, and John Machuzak
- SRTC - Bill Holtzcheiter, Frank Smith III
- Ames - Glenn Bastiaans
- INEEL- Tom Thomas

Collaboration Type: Mission directed
Fiscal Year: 2000
Collaborator: (see description)
Collaborating Organization: (see description)

Description: The objectives of the project are to develop new real-time sensors for characterizing glass melts in high level waste (HLW) and low activity waste (LAW) melters, and to understand the scientific basis and bridge the gap between glass melt model data and melter performance. A basic goal is to characterize glass melts in-situ with the new diagnostic capability so that data will represent the actual melt's behavior. The work will be closely coupled to the needs of the Defense Waste Processing Facility, West



Experimental setup for measuring the viscosity inside a melter. The represents the first time that a possibility for such a measurement has ever been demonstrated in real-time. Mullite waveguide shown going down into furnace with pressure sensor connection just below miter bend. Flanged window end of brass waveguide is connected to a hose for pressurizing waveguide with nitrogen when the mullite end of the waveguide is immersed in the glass. Millimeter-wave pyrometer electronics are inside the aluminum box in the background on right. [see Project #81897, renewal of #65435]

Valley Demonstration Project, and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. The project is a collaboration between the MIT Plasma Science and Fusion Center, PNNL, and the Savannah River Technology Center. In addition, discussions are in progress with Tom Thomas of the Tanks Focus Area regarding the possibility of demonstrating with the TFA.

Collaboration Type: Program interaction
Fiscal Year: 1999
Collaborator: Tom Thomas
Collaborating Organization: Tanks Focus Area

Description: Collaborations with other laboratories are being exploited to field test the research accomplished by this project. For example, a field test at TFA request was carried out at the Clemson Environmental Technology Laboratory (CETL) in August 2000 on a pilot scale melt test of an INEEL glass surrogate. An open invitation exists from CETL for additional joint experiments. The EMSP support is thus leveraged by the field test facilities being provided by TFA.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborating Organization: Tanks Focus Area

Geochemistry

Project: 60403

Title: Phase Chemistry of Tank Sludge Residual Components
PI: Dr. James L. Krumhansl *Institution:* Sandia National Laboratories - Albuquerque

Description: Because it is not possible to recover all of the contaminated sludge from the bottoms of decommissioned waste storage tanks, a credible model for the release of radionuclides from residual sludge is needed. Those sludge components most likely to retain radionuclides will be identified and synthesized. Radionuclide sorption and desorption will also be studied. AFM and STM studies will provide a firm atomistic explanation for the observed interactions between the sludge, solutions, and radionuclides. This understanding will be used to develop a quantitative radionuclide release source term for use in the performance assessment calculations.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Larry Bustard
Collaborating Organization: TFA

Inorganic Chemistry

Project: 73778 (Renewal of Project 60296)

Title: Research Program to Investigate the Fundamental Chemistry of Technetium
PI: Dr. David K. Shuh *Institution:* LBNL

Description: This project addresses the fundamental solution chemistry of technetium (Tc) in the waste tank environment, and the stability of Tc in various waste forms. A separate facet of this project is the search for lower valent forms of Tc that may be incorporated in various waste forms for long term storage. Collaborated with PNNL as a participant (technical expert) at Technetium Chemistry workshop review panel assessing tank technetium removal/disposition options.

Collaboration Type: Consulting *Fiscal Year:* 1998
Collaborating Organization: PNNL

Project: 73832 (Renewal of Project 55229)

Title: The NOx System in Homogeneous and Heterogeneous Nuclear Waste
PI: Dr. Dan Meisel *Institution:* University of Notre Dame

Description: This project, a collaborative ANL/PNNL effort, studies processes of the title system as it relates to the chemistry in high level liquid nuclear waste (HLW). The program is structured to transfer the information directly to the Hanford site operators (via "Organic Aging Studies, *PI:* Don Camaioni, PNNL). Our activity is also closely coordinated with another EMSP project ("Interfacial Radiolysis", *PI:* Thom Orlando, PNNL) and we include below our results that relate directly to that project. We determined the redox potential of the NO32- radical and its possible conversion to NO radical rather than to NO2. We also determined the redox potential of the analogous NO22- radicals because this parameter will determine whether such a conversion is possible. We concluded that both NO2 and NO radicals are important intermediates in HLW and the relative importance will depend on the concentration of nitrite in the waste tank. As a consequence we will coordinate our activity with a recently awarded EMSP project that focuses on NO chemistry and its derivatives ("Reactivity of Peroxynitrite", *PI:* Sergei Lymar, BNL).

Collaboration Type: Mission directed *Fiscal Year:* 1999
Collaborator: Sergei Lymar, Thom Orlando
Collaborating Organization: BNL, PNNL

Materials Science

Project: 60020

Title: Stability of High-Level Waste Forms
PI: Dr. Theodore M. Besmann *Institution:* ORNL

Description: Models of phase relations and liquidus temperatures developed in this EMSP program are being used to evaluate test results from the Tanks Focus Area Immobilization Program Waste Loading Improvements in High and Low Activity Glasses and Waste Form Product Acceptance Testing. The focus at this time is on conditions where crystallization occurs in glass processing. By applying models to the test data, an understanding of crystallization and how to avoid it may be obtained.

Collaboration Type: Joint interaction *Fiscal Year:* 1999
Collaborator: John Vienna
Collaborating Organization: PNNL

Description: Experimental studies of phase relations in the sodium oxide-boron oxide-uranium (VI) oxide system are being run in this EMSP program because there is no information in the literature. This data is needed for modeling actinide behavior in glasses. The results of these tests are also being spun off to assist the Uranium-233 Disposition Program of the Office of Fissile Materials Disposition (DOE/MD). They are considering dissolution of uranium oxide in sodium borate or boron oxide as an option for Uranium-233 disposition. As experimental data is produced, it is made available to the Uranium-233 Program to assist in their development of a flow sheet. Because of the dearth of information on this system, it is not surprising that any information that is produced may be applied in different activities.
Collaboration Type: Joint interaction *Fiscal Year:* 1998
Collaborator: Charles Forsberg
Collaborating Organization: ORNL

Description: We have supported efforts on increasing waste loading in glass. We performed computations modeling a waste glass formulation to predict precipitation of a crystalline phase, nepheline, which destabilizes the glass.

Based on this work a compositional maps at different temperatures indicating ranges under which nepheline is likely to precipitate was developed. We also produced liquidus temperature plots as a function of composition. Results indicates that nepheline formation can be suppressed at high silica and/or boria contents.
Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: John Vienna, Pavel Hrma and Hong Li
Collaborating Organization: Tanks Focus Area Immobilization Project Waste Loading Optimization Task; PNNL

Description: The objective of the project is to use a new approach to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility. We have been supporting efforts on increasing waste loading in glass. We have performed computations modeling a waste glass formulation to predict precipitation of a crystalline phase, nepheline, which destabilizes the glass. The results indicated compositional regions that promoted or suppressed precipitation. These can be used to help design glass compositions that will allow increased waste loading.
Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: John Vienna, Pavel Hrma, and Hong Li
Collaborating Organization: TFA Immobilization Project (PNNL)

Project: 60362

Title: Ion-Exchange Processes and Mechanisms in Glasses
PI: Dr. B. Peter McGrail *Institution:* PNNL

Description: The objective of this project is to develop an understanding of the processes and mechanisms controlling alkali ion exchange and to correlate the kinetics of the ion-exchange reaction with glass structural properties. The fundamental understanding of the ion-exchange process developed under this study will provide a sound scientific basis for formulating low exchange rate glasses with higher waste loading, resulting in substantial production and disposal cost savings.

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: D.K. Shuh
Collaborating Organization: LBNL

Project: 65408

Title: Mechanisms and Kinetics of Organic Aging in High-Level Nuclear Wastes
PI: Dr. Donald M. Camaioni *Institution:* PNNL

Description: Highly radioactive wastes stored at Hanford and Savannah River DOE sites have unresolved questions relating to safety of the stored waste, as well as needs for safe, effective, and efficient waste processing to minimize the volume of high-level waste (ULW) streams for disposal. Dr. Camaioni has supplied technical input on tank waste issues to Hanford Site contractor personnel. Discussions with CH2M Hill Hanford Group, Inc. regarding the chemistry of polychlorinated biphenyls in Hanford tank wastes have taken place. DOE is interested in knowing the extent to which PCBs may undergo radiation and chemical destruction.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: Joe Meacham
Collaborating Organization: CH2M Hill Hanford Group, Inc

Project: 73748 (Renewal of Project 60345)

Title: New Metal Niobate and Silicotitanate Ion Exchagers: Development and Characterization
PI: Yali Su *Institution:* PNNL

Description: Research performed on this EMSP project has led to a mission-directed, joint interaction between researchers on this program and end users of the CST at SRS. EMSP principal investigators at PNNL and SNL have been asked to evaluate the effect of temperature excursions (below 120 °C) on the performance and material properties of the CST. This information will be used by DOE to select the best process for Cs separation at SRS. In addition, the data provided by PNNL and SNL will be used to develop engineering solutions process upsets that result in minor temperature excursions. This is an EM-funded program.

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborating Organization: CST and SRS

Description: The Tanks Focus Area is managing the research and development program for the Salt Processing Project at the SRS. Three candidate cesuim removal technologies are being considered for down selection: Crystalline Siliconate Non-Elutable Ion Exchange (CST), Caustic Side Solvent

Extraction (CSSX), and Small Tank Tetraphenylborate Precipation (STTP). The research conducted under this EMSP project is directly applicable to the CST process. The principal investigator for this project is being funded by the Tanks Focus Area to bring their expertise and creativity to the development and selection process for this critical DOE project.

Collaboration Type: Consulting *Fiscal Year:* 2001
Collaborating Organization: Savannah River Salt Processing Project and Tanks Focus Area

Description: This project, a collaborative PNNL/SNL/UC Davis effort, identifies new waste forms and disposal strategies specific to crystalline silicotitanate (CST) secondary waste that is generated from Cs and Sr ion exchange processes. The goals of the program are to reduce the costs associated with CST waste disposal, to minimize the risk of contamination to the environment during CST processing, and to provide DOE with technical alternatives for CST disposal. The technical objectives of the proposed work are to fully characterize the phase relationships, structures, and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and to establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry. Collaborations for each associated task are as follows:

Task: Evaluation of thermally converted CST and structure/properties relationship studies of silicotitanates and related compounds.
- Y. Su, E. Bitten, and D. McCready, PNNL (Program interaction).

Task: Hydrothermal synthesis silicotitanates and related ion exchanger material.
- Nenoff and M. Nyman, SNL (Program interaction).

Task: Thermochemical studies of silicotitanates and related ion exchanger materials.
- A. Navrotsky and H. Xu, UC Davis (Program interaction).

Task: Single crystal growth.
- Dr. R. Roth, NIST and The Viper Group (Consulting).

Task: Radiation damage studies of silicotitanates.
- Professor R. Ewing, University of Michigan (Consulting).

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: (see description)
Collaborating Organization: (see description)

Description: In this program, we at SNL have developed both a silicotitanate ion exchanger and a new Metal Niobate Ion exchanger. Both are excellent at divalent cation selectivity. The Metal Niobate Ion Exchanger shows exceptional selectivity for divalent cations over monovalent cations.

Though this is in the experimental stage (and NOT yet an optimized material), we do see great potential for this material is a variety of applications around the DOE complex. This material is currently submitted for a patent. We are in discussions with INEEL, about simulant testing of these non-optimized materials for various DOE complex wastes.

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborator: Dean Peterman
Collaborating Organization: INEEL

Project: 73750 (Renewal of Project 54672)

Title: Radiation Effects in Nuclear Waste Materials
PI: Dr. William J. Weber *Institution:* PNNL

Description: The PI was requested to assist in evaluating potential radiation-induced failure of protective glass globes for lights in the in-tank camera systems for Tank 101-SY at Hanford. Unexplained failure of two globes had raised some safety concerns. Working with Lockheed Martin Hanford Co. staff, an interim testing program was designed for the protective glass globes, a procedure to minimize potential failure (change globes frequently) was advised, and some preliminary measurements and evaluations were conducted on irradiated globes. No permanent solution was developed as of yet.

Collaboration Type: Consulting *Fiscal Year:* 1998
Collaborator: Scott M Werry
Collaborating Organization: Lockheed Martin Hanford Co.

Project: 73762 (Renewal of Project 54691)

Title: Radiation Effects on Sorption and Mobilization of Radionuclides during Transport through the Geosphere
PI: Dr. Lu-Min Wang *Institution:* University of Michigan

Description: Successful, demonstrated containment of radionuclides in the near-field can greatly reduce the complexity of the performance assessment analysis of a geologic repository. The chemical durability of the waste form, the corrosion rate of the canister, and the physical and chemical integrity of the back-fill provide important barriers to the release of radionuclides. However, near-field containment of radionuclides depends critically on the behavior of these materials in a radiation field. Continued efforts in this regard include the evaluation of the capabilities of the uranyl phases to incorporate and retard release of important radionuclides: Np-237, Se-79, Tc-99, and I-129.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Professor Peter Burns
Collaborating Organization: Notre Dame

Description: The objective of this research program has been to evaluate the long-term radiation effects in materials used in processing high-level nuclear waste or materials in the near-field of a nuclear waste repository. This program has established the following collaborations:

Dr M. L. Balmer (PNNL) and Dr. T. M. Nenoff (SNL) - EMSP Project 60345

- We have studied radiation effects on samples associated with the development of new silicotitanate waste form development provided by their research groups and provided data to them.

Dr. G. Liu (ANL) - EMSP Project 55367

- Information and experience exchanged on radiation damage studies.

Prof. A. Clearfield (Texas A&A University) - EMSP Project 54735

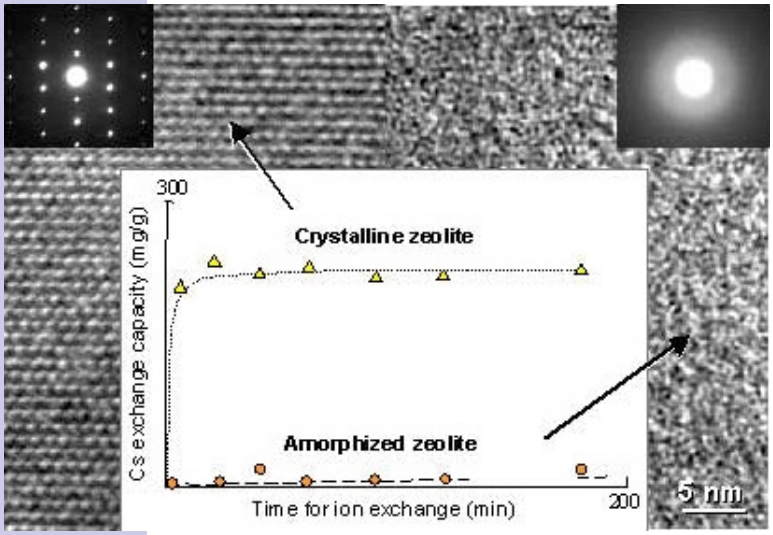
- We have obtained silicotitanate samples synthesized by Prof. Clearfield and conducted a preliminary study on radiation effects in the sample.

Dr. W.J. Weber (PNNL) - EMSP Project 54672

- Information and experience exchange on radiation damage studies.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: (see descriptions)
Collaborating Organization: (see descriptions)

Description: The principal sources of radiation in high-level nuclear waste are ?-decay of the fission products (e.g., 137Cs and 90Sr) and ?-decay of the actinide elements (e.g., U, Np, Pu, Am and Cm). Both types of radiation can cause important chemical and physical changes in materials (e.g., increase in leach rates, volume expansion, solid state radiolysis and bubble formation, and reduced cation exchange capacity). The radiation-solid interactions are complex because they involve a combination of ionization effects due to electronic excitations and ballistic effects due to elastic collisions. The strength of the radiation field decreases dramatically with time, and the type of radiation damage varies over time (?-decay damage due to actinides dominates over ?-decay effects due to fission products with increasing time due to the long half-lives of the actinides). Further, the radiation effects vary as a function of the type of solid (ionic vs. covalent), the type of damage (inelastic vs. elastic interactions), the temperature of the irradiation, and the kinetics of the annealing mechanisms. Ongoing collaborative work includes that accomplished with Peter Burns of Notre Dame University on the fate of fission products released by the corrosion and alteration of spent nuclear fuel.



Effect of solid-state amorphization on Cs exchange capacity of zeolite. As demonstrated by University of Michigan, zeolite lost 95% of its Cs exchange capacity after solid-state amorphization. [see Project #73762, renewal of #54691]

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: Professor Peter Burns
Collaborating Organization: Notre Dame

Project: 73976 (Renewal of Project 55110)

Title: Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes
PI: Dr. Delbert E. Day *Institution:* University of Missouri-Rolla

Description: Drs. Bruce Bunker and Lou Balmer provided information for sludge compositions in various tank farms, especially for wastes considered good candidates for iron phosphate glasses. Iron phosphate glasses were provided to Dr. Bill Weber for radiation damage studies. Dr. Pavel Hrma provided useful data for borosilicate glasses.
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Drs. Bruce Bunker, Lou Balmer, Bill Weber, & Pavel Hrma
Collaborating Organization: PNNL

Description: We are collaborating on a project whereby we are developing an iron phosphate glass containing INEEL waste (calcine) that will eventually be melted in the cold wall induction furnace in Russia. This collaboration is an important step in moving the interesting iron phosphate glasses out of the laboratory into the real world of "large scale" or practical production.
Collaboration Type: Mission directed *Fiscal Year:* 2001
Collaborator: Dirk Gombert
Collaborating Organization: INEEL

Description: Dr. William G. Ramsey provided information for sludge compositions and evaluated iron phosphate glasses which contained uranium and plutonium. Undergraduate and graduate students from UMR worked part time at the Savannah River Laboratory with Drs. Carol Jantzen, William Miller, and others.
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Drs. William G. Ramsey, Carol Jantzen, & Wiiliam Miller
Collaborating Organization: Westinghouse Savannah River Company

Description: Certain high level wastes (HLWs) are not well suited for vitrification in borosilicate (BS) glasses because they contain components such as phosphates that are poorly soluble in a BS host matrix. The waste loading must be significantly reduced if one is to successfully vitrify such problematic wastes in a BS glass. Iron phosphate glasses offer a technically feasible and cost effective alternative to borosilicate glasses for vitrifying such HLWs. The main objective of the project was to investigate the atomic structure-property relationships, and glass forming and crystallization characteristics, of these iron phosphate glasses and glasses containing nuclear waste components. Other physical properties such as density and thermal expansion were studied. Collaborations for each associated task are as follows:

Task: X-Ray Absorption Spectroscopy (EXANES/EXAFS) at the Stanford Synchrotron Radiation Laboratory

- Drs. David Shuh, Jerry Bucher, N.M. Edelstein, and Corwin Booth, LBNL
- Dr. Pat Allen, LLNL

Task: Neutron and High Energy X-Ray Scattering

- Drs. Marie-Louise Saboungi, Yaspal Badyal, and Dean Heaffner, The Division of Materials Science, Intense Pulsed Neutron Source, and The Advanced Photon Source, ANL

Task: Raman Spectroscopy

- Dr. Marcos Grimsditch, Division of Materials Science, ANL
- Dr. Andrea Mogus-Milankovic, Ruder Boskovic Institute, Croatia

Task: Electron Spin Resonance Studies

- Dr. David Griscom, Naval Research Laboratory

Task: Electrical properties (conductivity, loss, and dielectric constant)

- Dr. Andrea Mogus-Milankovic, Ruder Boskovic Institute, Croatia

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: (See description)
Collaborating Organization: (See description)

Description: Drs. David Shuh, N. M. Edelstein, and Corwin Booth of the Actinide Chemistry Division provided experimental and theoretical support for x-ray absorption (EXAFS/XANES) studies conducted at the Stanford Synchrotron Radiation Laboratory (SSRL). Personnel from University of Missouri-Rolla visited both SSRL and LBNL to conduct experiments and to be trained in data analysis.
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Drs. David Shuh, N. M. Edelstein, & Corwin Booth
Collaborating Organization: LBNL

Description: Drs. Marie-Louise Saboungi and Yaspal Badyal provided experimental and theoretical support for neutron scattering studies conducted at the Intense Pulsed Neutron Source (IPNS). Dr. Dean Heaffner provided access to the Advanced Photon Source (APS) for high energy x-ray scattering studies and Dr. Marcos Grimsditch provided experimental and theoretical support for Raman spectral studies. Personnel from UMR visited ANL to conduct experiments and to be trained in data analysis.
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Drs. Marie-Louise Saboungi, Yaspal Badyal, Dean Heaffner, & Marcos Grimsditch
Collaborating Organization: ANL

Description: We have recently developed an alternative waste form based on a new family of iron-phosphate glasses which appear to be well suited for many waste feeds, especially those which are incompatible with borosilicate glasses. This previous work at the University of Missouri-Rolla, done in

collaboration with scientists from PNNL, Westinghouse Savannah River Laboratory, and LBNL, strongly suggests that iron phosphate glasses are a low cost and highly, effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. Recently, Dr. Pat Allen of LLNL provided experimental and theoretical support for additional x-ray absorption (EXAFS/XANES) studies.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dr. Pat Allen
Collaborating Organization: LLNL

Description: A thorough investigation of the structure and properties of iron-phosphate glasses and their wasteforms in the first part of this project has been made. Part of this work entailed the recruitment of top scientists at LBNL and ANL to study the specific structural aspects of these glasses. It is anticipated that this effort will continue in the future.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborating Organization: LBNL and ANL

Description: We have recently developed an alternative waste form based on a new family of iron-phosphate glasses which appear to be well suited for many waste feeds, especially those which are incompatible with borosilicate glasses. This previous work at the University of Missouri-Rolla, done in collaboration with scientists from PNNL, Westinghouse Savannah River Laboratory, and LBNL, strongly suggests that iron phosphate glasses are a low cost and highly, effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. Dr. Andrea Mogus-Milankovic of Ruder Boskovic Institute in Zagreb, Croatia, measured Raman/IR spectra and AC/DC conductivity of these iron phosphate glasses.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. Andrea Mogus-Milankovic
Collaborating Organization: Ruder Boskovic Institute, Zagreb, Croatia

Description: Two groups in Japan have become interested in our research on iron phosphate glasses. As part of a program on spent fuel recycling supported by the Japanese government, we were contacted by IHI (Ishikawajima-Harima Heavy Industries). IHI is coupled with IRI (Institute of Research and Innovation) to investigate alternative glasses that could be used to vitrify the waste from fuel recycling and have made the decision to study iron phosphate glasses for that purpose. We gave them a briefing on our work in Tokyo in Nov 2000 and then a delegation (six persons) from both groups visited UMR in Feb 2001. We are working with them on an unofficial basis in reviewing their research plan, sharing our technical data, teaching them how to melt iron phosphate glasses, and reviewing their research results. We are pleased that there is interest in Japan in the iron phosphate glasses and that they see value in evaluating these glasses for their use.

Collaboration Type: Consulting *Fiscal Year:* 2001
Collaborating Organization: Ishikawajima-Harima Heavy Industries and Institute of Research and Innovation

Description: We have recently developed an alternative waste form based on a new family of iron-phosphate glasses which appear to be well suited for many waste feeds, especially those which are incompatible with borosilicate glasses. This previous work at the University of Missouri-Rolla, done in collaboration with scientists from PNNL, Westinghouse Savannah River Laboratory, and LBNL, strongly suggests that iron phosphate glasses are a low cost and highly, effective alternative to borosilicate glasses for vitrifying selected nuclear wastes. Dr. David Grisscom conducted Electron Spin Resonance spectral and Gas Evolved Mass Spectroscopy studies on iron phosphate glasses provided by University of Missouri-Rolla.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dr. David Grisscom
Collaborating Organization: Naval Research Laboratory

Separations Chemistry

Project: 54735

Title: Development of Inorganic Ion Exchangers for Nuclear Waste Remediation
PI: Dr. Abraham Clearfield *Institution:* Texas A&M University at College Station

Description: This research is concerned with the development of highly selective inorganic ion exchangers for the removal of primarily Cs+ and Sr2+ from nuclear tank waste and from groundwater. In this study, we will probe the origins of selectivity through detailed structural studies, and the thermodynamics of the ion exchange processes. I am working with David Hobbs, whose group is testing our exchangers for removal of Sr, Pu, Np from SR tank waste.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: David Hobbs
Collaborating Organization: Savannah River

Description: This research is concerned with the development of highly selective inorganic ion exchangers for the removal of primarily Cs+ and Sr2+ from nuclear tank waste and from groundwater. In this study, we will probe the origins of selectivity through detailed structural studies, and the thermodynamics of the ion exchange processes. The compounds to be synthesized may have cavity or tunnel structures, layer structures, or be amorphous gels. A key component to the development of this research has been the collaboration with a group of scientists at the Institute for Sorption and Problems of Endoecology (ISPE), in Kiev, Ukraine, where they have been concerned with remediation of the Chernobyl zone. Porous carbons treated with inorganic ion exchangers for soil and groundwater remediation have been devised, which sorb pesticides, Regicides, and heavy metals.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborating Organization: Institute for Sorption and Problems of Endoecology (ISPE), Kiev, Ukraine

Project: 54996

Title: Ionizing Radiation Induced Catalysis on Metal Oxide Particles
PI: Dr. Michael A. Henderson *Institution:* PNNL

Description: This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. We have shown that ionizing radiation can be used to catalytically destroy organic chelating agents, such as EDTA, whose presence in high-level waste streams hinder the removal of radionucleii by ion exchange. Our studies have shown that gamma irradiation of titanium dioxide suspensions destroy the chelating ability of EDTA by decomposing it to smaller organic molecules. This has been demonstrated for both free EDTA in solution and for solutions of EDTA complexed to strontium. Present efforts are aimed at determining the mechanism by which EDTA is destroyed and the feasibility of using this process for treating high-level mixed waste.
Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: Abhaya K. Datye; Professor Miguel E. Castro
Collaborating Organization: University of New Mexico; University of Puerto Rico

Project: 73803 (Renewal of Project 55087)

Title: Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation
PI: Dr. Bruce A. Moyer *Institution:* ORNL

Description: The PI has had an ESP project to develop processes for removal of fission products from high-level waste. The understanding gained from this EMSP task enabled the PI and his co-workers to solve a critcal problem in FY 1998. The understanding has also been useful in subsequent development through FY 2000. Although the carryover in the ESP budget is now exhausted, in the past quarter the PI was able to spend a few hours presenting results in a management briefing to Steve Richardson, DOE-ORO, and ORNL management. In addition, some ESP hours were spent presenting input to the National Academy of Sciences, which is reviewing the salt disposition situation at the SRS. This input consisted of answers to five questions regarding the status and viability of the process for removing cesium from the high-level waste being stored at the SRS. The fundamental information obtained on cesium extraction equilibria was used indirectly in the presentation to Richardson and in the input to the National Academy. As a result, Richradson was excited about the possibility that the SRS is going to provide funds for further testing of the alkaline-side CSEX process. His reaction was to ask how he could facilitate ORNL being named lead laboratory for this testing. The NAS has not issued its report to the PI's knowledge, but it is likely based on its interim report issued in October that it will recommend that the SRS expend funds to accelerate the development of the process.
Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborating Organization: EM-50 Efficient Separations and Processing (ESP) Crosscutting Program

Description: In order to supply the committee with data needed for its report to the USDOE Under Secretary, this project provided members of the team with information concerning the recent work, research, and performance accomplished in a presentation by P. V. Bonnesen in Nov. 1999. In Jan. and Mar. 2000, additional detailed information in the form of answers to written questions by committee members was provided as well. This information was incorporated into a WSRC report entitled "SRS High-Level Waste Salt Disposition Responses to NRC Questions of 1-11-00." In Aug. 2000, the committee issued its report based in part on this information, urging further testing of the CSEX process.

Collaboration Type: Mission directed *Fiscal Year:* 2000

Collaborating Organization: National Academy of Sciences, National Research Council Committee on Salt Disposition at the SRS

Description: The Tanks Focus Area is managing the research and development program for the Salt Processing Project at the SRS. Three candidate cesuim removal technologies are being considered for down selection: Crystalline Siliconate Non-Elutable Ion Exchange (CST), Caustic Side Solvent Extraction (CSSX), and Small Tank Tetraphenylborate Precipation (STTP). The research conducted under this EMSP project is directly applicable to the CSSX process. The principal investigator for this project is being funded by the Tanks Focus Area to bring their expertise and creativity to the development and selection process for this critical DOE project.

Collaboration Type: Consulting *Fiscal Year:* 2001

Collaborating Organization: Savannah River Salt Processing Project and Tanks Focus Area

Description: Due to the strong interaction with Westinghouse Savannah River Corp., Tanks Focus Area representatives were routinely kept informed. Members of the TFA continue to praise the progress made, encourage further work, and mediate interaction with the SRS. This past August, a large TTP was submitted from ORNL to the TFA to cover the demonstration and testing of the CSEX process for the SRS in FY 2001. This TTP has been funded at the level of $1.8M. ANL will receive $0.85M, and the SRTC will receive $3.2M. The ORNL, ANL, and SRTC teams will work closely with each other.

Collaboration Type: Program interaction *Fiscal Year:* 2000

Collaborating Organization: EM-50 Tanks Focus Area

Description: A combined effort at Oak Ridge, Pacific Northwest, and Argonne National Laboratories and the University of Tennessee is proposed to design, synthesize, and characterize the next generation of crown ethers for metal-ion separations applicable to USDOE's environmental needs. This research combines three inter-dependent projects dealing with 1) molecular mechanics and ligand design, 2) solvent-extraction properties, and 3) resin-immobilized crowns. Despite impressive developments in the chemistry of crown ethers, factors such as the need for polar environments and "forcing" conditions, weak efficiency, and dependence on matrix anions limits

their potential in separations. Exploiting advances in molecular mechanics, this research seeks accelerated progress through ligand design and synthesis coupled with testing of predictions via structural, spectroscopic, and separation techniques. New crown compounds will be studied in solvent-extraction and polymer systems, emphasizing ion-exchange features. Selectivity principles governing the binding of such ions as Li+, Cs+, Sr2+, and Ra2+, all of which have been identified as contaminants at USDOE sites, will be investigated. The partner laboratories have world-recognized programs in the area of crown ethers, solvent extraction, and ion exchange. Their cooperation under this research represents an unusual and extremely effective combination of unique resources. As such, the US DOE Independent Project Evaluation Committee for cesium-removal technology selection for high-level tank waste at the SRS recently provided members of this team with information concerning the process and its performance.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborating Organization: US DOE Independent Project Evaluation Committee for cesium-removal technology selection for high-level tank waste at the SRS

Description: Customer evaluation of the alkaline-side CSEX process as an alternative technology for replacement of the in-tank precipitation process was the main driving force behind this collaborative effort with Westinghouse Savannah River Corporation. A successful evaluation will result in further development, scale-up, demonstration, and pilot-scale testing. Ultimately, the main goal of this effort is implementation in a billion-dollar plant. At present, test results have been very positive, and the CSEX process appears competitive with current alternative technologies.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborating Organization: Westinghouse Savannah River Corporation

MIXED WASTE

Actinide (Heavy Element) Chemistry

Project: 60370

Title: Rational Design of Metal Ion Sequestering Agents
PI: Dr. Kenneth N. Raymond *Institution:* LBNL

Description: An enormous amount of radioactive and toxic chemical waste remains at over one hundred sites managed by the Department of Energy. Despite the investment of large sums major goals associated with the cleanup remain unmet. It is our thesis that economically practical accomplishments of these tasks will require technology not yet available. Basic studies of the sequestration of the relevant toxic metal ions is required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment, and minimize the production of secondary wastes. This research group has for many years led the development of new, metal-ion-selective sequestering agents. In what has been described as the first rational synthesis of such an agent, decontamination for Pu4+

have been developed. What is now proposed is the full thermodynamic and structural characterization of the metal-ligan systems that form the basis for rational metal-ion-specific ligand design. This will provide the basis for technologies targeted towards the separation and immobilization of hazardous metal ions. This project encompasses the synthesis of new materials, the physical characterization and evaluation of those materials, and the evaluation (and subsequent improvement) of these materials for interface to applied separation technologies.

Following these guidelines, Drs. Barbara Smith and Gordon Jarvinen of LANL recently synthesized and evaluated water-soluble chelating polymers, based on hydroxypyridinone and terephthalamide ligands attached to polyethyleneimine (PEI), as sequestering agents for uranyl, Pu, and Am.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Drs. Barbara Smith and Gordon Jarvinen
Collaborating Organization: LANL

Description: An enormous amount of radioactive and toxic chemical waste remains at over one hundred sites managed by the Department of Energy. Despite the investment of large sums major goals associated with the cleanup remain unmet. It is our thesis that economically practical accomplishments of these tasks will require technology not yet available. Basic studies of the sequestration of the relevant toxic metal ions is required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment, and minimize the production of secondary wastes. This research group has for many years led the development of new, metal-ion-selective sequestering agents. In what has been described as the first rational synthesis of such an agent, decontamination for Pu4+ have been developed. What is now proposed is the full thermodynamic and structural characterization of the metal-ligan systems that form the basis for rational metal-ion-specific ligand design. This will provide the basis for technologies targeted towards the separation and immobilization of hazardous metal ions. This project encompasses the synthesis of new materials, the physical characterization and evaluation of those materials, and the evaluation (and subsequent improvement) of these materials for interface to applied separation technologies.

Following these guidelines, Dr. Ben Hay of PNNL recently provided atomic coordinates from X-Ray crystal structures of actinide complexes of hydroxypyridinone, terephthalamide, and other ligands. This data is used in high level computational studies directed toward rational design of new actinide sequestering agents.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Dr. Ben Hay
Collaborating Organization: PNNL

Description: This project addresses the fundamental issues and requirements for developing hazardous metal ion separation technologies applicable to the

treatment and disposal of radioactive waste. Our research encompasses the following areas: the design and synthesis of metal ion specific sequestering ligands, structural and thermodynamic investigations of these ligands and the complexes formed with targeted metal ions, and the development and incorporation of these ligands into applied separation technologies as highly effective materials for hazardous metal ion decontamination. This interaction has provided direct structural, thermodynamic and electrochemical studies of plutonium complexes.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Dr. Heino Nitsche
Collaborating Organization: LBNL

Description: An enormous amount of radioactive and toxic chemical waste remains at over one hundred sites managed by the Department of Energy. Despite the investment of large sums major goals associated with the cleanup remain unmet. It is our thesis that economically practical accomplishments of these tasks will require technology not yet available. Basic studies of the sequestration of the relevant toxic metal ions is required in order to develop processes that will treat effluents sufficiently well to allow direct release into the environment, and minimize the production of secondary wastes. This research group has for many years led the development of new, metal-ion-selective sequestering agents. In what has been described as the first rational synthesis of such an agent, decontamination for Pu4+ have been developed. What is now proposed is the full thermodynamic and structural characterization of the metal-ligan systems that form the basis for rational metal-ion-specific ligand design. This will provide the basis for technologies targeted towards the separation and immobilization of hazardous metal ions. This project encompasses the synthesis of new materials, the physical characterization and evaluation of those materials, and the evaluation (and subsequent improvement) of these materials for interface to applied separation technologies.

Following these guidelines, Dr. Glen Fryxell of PNNL has recently synthesized ligands and developed a general synthetic methods to apply a broad range of coordinating groups as actinide sequestering agents in Self-Assembled Monolayers on Mesoporous Silica.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Dr. Glen Fryxell
Collaborating Organization: PNNL

Analytical Chemistry & Instrumentation

Project: 54751

Title: High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste
PI: Dr. Mark M. Pickrell *Institution:* LANL

Description: The objective of the project is to research the basic plasma physics necessary to develop a high fluence neutron source based on the inertial

Two commercial partners have applied for a license for the High Fluence Neutron Source, shown here in the laboratory. [see Project #54751]

electrostatically confined (IEC) plasma. An intense neutron source directly addresses the capability to characterize nuclear materials under difficult measurement conditions. Some of the applications for Environmental Management are the characterization of TRU wastes for WIPP, the measurements of residues prior to stabilization and disposal, the measurements of cemented or vitrified wastes, the measurement of spent nuclear fuel, and the measurement of high level wastes. Collaborations with the INEEL and the National Spent Nuclear Fuels Program to produce a neutron source for MDAS or other systems being developed by the INEEL.

Collaboration Type: Mission directed
Fiscal Year: 1999
Collaborator: Jerry Cole
Collaborating Organization: INEEL

Project: 55171

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

PI: Dr. Digby D. MacDonald *Institution:* Pennsylvania State University

Description: The principal objective of this project is to develop new, innovative methods for accurately measuring parameters that characterize corrosion processes in the Super Critical Water Oxidation SCWO technology. SCWO is a promising approach for destroying highly toxic organic waste (including physiological agents) and for reducing the volume of DOE's low-level nuclear waste. The lack of experimental techniques for accurately monitoring important parameters, such as pH, corrosion potential and corrosion rate, has severely hampered the development of a quantitative understanding of the degradation of materials in the extraordinarily aggressive SCWO environment. Specific accomplishments are as follows:

- As a result of our three-year effort, we have developed new chemical and corrosion sensors for use in high subcritical and supercritical aqueous environments. The precision and readability of the sensors have been significantly improved over previous systems and the fundamental thermodynamic and corrosion properties of supercritical aqueous system can now be properly measured over wide ranges of temperature and pressure.

- The novel flow-through yttria-stabilized zirconia (YSZ) pH electrode and flow-through external reference electrode have been developed and evaluated. Potentiometric measurements have been carried out to determine the pH of dilute hydrochloric acid at temperatures up to 400°C.

- The association constant of hydrochloric acid was evaluated from measured potentiometric data and used to judge the accuracy of the pH measuring system. The results have been compared with available literature data and good agreement between experimentally measured and literature data is obtained. The data demonstrate that the electrochemical probes developed in this work are capable of providing potential measurements of sufficient accuracy that quantitative potentiometric studies on aqueous solutions at temperatures above the critical temperature are now possible.

- Three-electrode electrochemical noise (EN) sensors have been developed for measuring corrosion rate in subcritical and supercritical environments. The EN sensors were tested in flowing aqueous solutions containing NaCl and HCl at temperatures ranging from 150° to 390°C, at a pressure of 25 MPa, and at flow rates from 0.375 ml/min to 1.00 ml/min. The noise records in the potential and coupling current from Type 304 stainless steel were recorded simultaneously.

- The inverse noise resistance was found to correlate very well with the measured corrosion rate at various temperatures and flow rates. At temperatures higher than 150°C, the corrosion rate was found to be proportional to the inverse noise resistance as required by the Stern-Geary relationship. Accordingly, noise resistance can be used to evaluate corrosion rate in these aggressive, low-density SCWO environments. Good agreement was found between the Stern-Geary constant evaluated via EN analysis and that determined via polarization measurements. To our knowledge, the work reported here represents the first determination of corrosion rate using electrochemical noise techniques in super critical aqueous solutions.

- A phenomenological model that was previously developed to account for the dependence of corrosion rate on temperature, and in particular to account for the passing of the corrosion rate through a maximum in the vicinity of the critical temperature, has been further developed to describe the variation of corrosion rate with pressure. The model has been used for Stone & Webster Engineering Co. to estimate the effect of pressure on corrosion rates of materials in the US Army's SCWO program for the destruction of chemical agents.

Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborator: Dr. George Engelhardt and Dr. Karen M. Garcia
Collaborating Organization: SRI International and INEEL

Project: 73844 (Renewal of Project 60231)

Title: Miniature Chemical Sensor Combining Molecular Recognition with Evanescent-Wave Cavity Ring-Down Spectroscopy

PI: Dr. Andrew C. R. Pipino *Institution:* National Institute of Standards & Technology - Maryland

Description: This project is developing a robust, rugged, portable, cost-effective sensor that has real-time chemical detection capabilities in gas, liquid, and semi-solid environments, and is therefore applicable in a variety of areas. Research is currently focused on vapor phase sensing of trichloroethylene (TCE) and perchloroethylene (PCE). This sensor has the ability to be tailored to a variety of constituents based on the end users needs. As such, an on-going collaboration is occurring with the Nevada Field Office to address their need for uranium detection in soils and groundwater.

Collaboration Type: Joint interaction *Fiscal Year:* 2001

Collaborator: John Jones and Bruce Crow

Collaborating Organization: DOE-NV

Description: This project is developing a robust, rugged, portable, cost-effective sensor that has real-time chemical detection capabilities in gas, liquid, and semi-solid environments, and is therefore applicable in a variety of areas. Research is currently focused on vapor phase sensing of trichloroethylene (TCE) and perchloroethylene (PCE). The researcher is working closely with the end user to develop a TCE sensor. Savannah River Technical Center has committed to field test this sensor upon its completion.

Collaboration Type: Mission directed *Fiscal Year:* 2001

Collaborator: Tim Smail

Collaborating Organization: Savannah River Technical Center

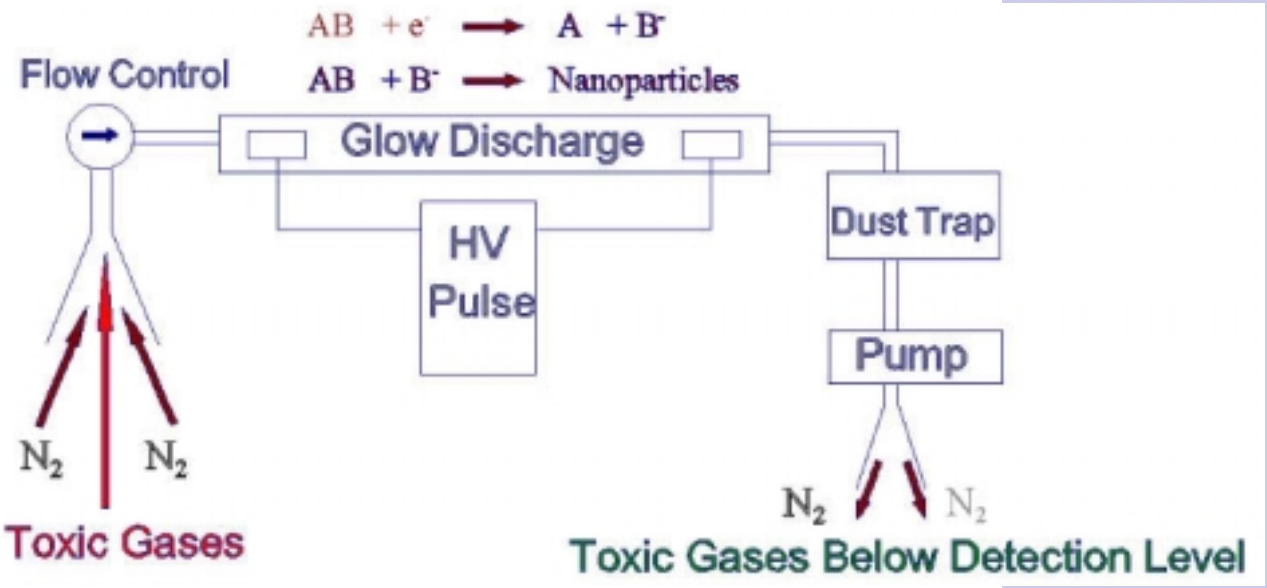
Engineering Science

Project: 54973

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

PI: Dr. Lal A. (ORNL) Pinnaduwage *Institution:* ORNL

Description: Removal of low-concentrations (below several percent) of volatile toxic compounds (VTCs) from contaminated air streams is encountered at DOE waste sites in two instances: (i) Off-gases resulting from air-stripping of contaminated soil and water. (ii) Effluent from the incineration of highly-concentrated combustible hazardous wastes. The objective of our research program is to develop a novel plasma chemical process for the destruction of VTC's in low- concentration waste streams. Discussions have been initiated to determine applicability of this work to Paducah groundwater treatment problems and assess site interest. Mr. Richards expressed considerable interest in this approach and noted the timeframe of availability (assuming follow-on funding for development) was compatible with site plans.



Remediation of Toxic Gas Streams. [see Project #54973]

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: Walt Richards
Collaborating Organization: Bechtel Jacobs Company, Paducah, KY

Inorganic Chemistry

Project: 54506

Title: Acid-Base Behavior in Hydrothermal Processing of Wastes
PI: Dr. Keith P. Johnston *Institution:* University of Texas at Austin

Description: A new technology, hydrothermal oxidation (also called supercritical water oxidation), is being developed to treat high level nuclear wastes. Nitrates are reduced to nitrogen; furthermore, phosphates, alumina sludge, and chromium are solubilized, and the sludge is reconstituted as fine oxide particles. A major obstacle to development of this technology has been a lack of scientific knowledge of chemistry in hydrothermal solution above 350 C, particularly acid-base behavior, and transport phenomena, which is needed to understand corrosion, metal-ion complexation, and salt precipitation and recovery. In an effort to understand these problems, collaborative work with LANL on experimentally treating tank waste with high temperatures is underway.
Collaboration Type: Joint interaction *Fiscal Year:* 1999
Collaborator: Steve Buelow
Collaborating Organization: LANL

Project: 54828

Title: Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water
PI: Dr. Charles A. Arrington, Jr. *Institution:* Furman University

Description: Current collaborative research efforts with LANL on the oxidative dissolution of chromium compounds found in Hanford tank waste sludge include focusing on the destructions of complexants and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions. Samples of chromium oxides and hydroxides with varying degrees of hydration are being characterized using Raman, FTIR, and XPS spectroscopic techniques. Kinetics of oxidation reactions at subcritical and supercritical temperatures are being followed by Raman spectroscopy using a high temperature stainless steel cell with diamond windows. In these reactions both hydrogen peroxide and nitrate anions are used as the oxidizing species with Cr(III) compounds and organic compounds as reducing agents. The work proposed by these LANL staff scientists is directed towards the destruction of complexants and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions. Experimental work was conducted at LANL during the summers and at Furman during the academic years.

Collaboration Type: Mission directed *Fiscal Year:* 1999
Collaborator: Steven Buelow and Jeanne Robinson
Collaborating Organization: LANL

Project: 59934

Title: Hazardous Gas Production by Alpha Particles in Solid Organic Transuranic Waste Matrices
PI: Dr. Jay A. LaVerne *Institution:* University of Notre Dame

Description: Hazardous gas production by the self-radiolysis of solid organic matrices, such as polymers and resins, containing radioactive material is a serious problem for waste management. Hydrogen is the most common hazardous gaseous product, although methane and ethane are possible, depending on the particular material. The yield of these products can be an order of magnitude different between alpha particles and gamma rays. Studies are in progress to estimate hazardous gas production in various solid matrices with different radiation. Fundamental knowledge on radiation chemical processes is being transferred to interested researchers at LANL.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborating Organization: Los Almos National Laboratory

Separations Chemistry

Project: 55103

Title: Utilization of Kinetic Isotope Effects for the Concentration of Tritium
PI: Dr. Gilbert M. Brown *Institution:* ORNL

Description: The objective of our work is to develop an electrochemically-based, cyclic process which can be used to remove tritium from contaminated water. We are developing methods for concentrating tritium from water based on large primary kinetic isotope effects in catalytic redox processes. H-T

discrimination occurs in an oxidation step involving a transition metal oxidant and small organic compounds containing oxidizable C-H or C-T bonds. Tritium is incorporated in the organic compound by an electrochemical reduction process in the presence of tritium contaminated water, but the protio-derivative is kinetically favored in the oxidation half-reaction. As a result of a cyclic oxidation-reduction process, tritium is enriched in the organic compound. The organic compound is chosen so that it does not readily exchange the tritium with groundwater.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: C.H. Ho, Douglas J. Lemme, Leon Maya, and Frederick V. Sloop, Jr.; Poonam M. Narula and Thomas J. Meyer
Collaborating Organization: ORNL; University of North Carolina at Chapel Hill

NUCLEAR MATERIALS

Engineering Science

Project: 60077

Title: Development of Nuclear Analysis Capabilities for DOE Waste Management Activities
PI: Dr. Cecil V. Parks *Institution:* ORNL

Description: Performance of an analysis of proposed experiments and prototypic spent fuel shipping and storage applications for the INEEL (INEEL). This analysis used the sensitivity analysis techniques developed under the EMSP project, in conjunction with other newly developed sensitivity and uncertainty analysis techniques, to determine whether a proposed set of critical experiments met the needs of INEEL for the validation of nuclear safety analysis software used in the design of shipping and storage applications for DOE-owned spent nuclear fuel. A preliminary report has been submitted to INEEL, and follow-up work is continuing.

Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: INEEL

Description: The objective of this project is to develop and demonstrate prototypical analysis capabilities that can be used by nuclear safety analysis practitioners to: (1) provide a more thorough understanding of the underlying physics phenomena that can lead to improved reliability and defensibility of safety evaluations; and (2) optimize operations related to the handling, storage, transportation, and disposal of fissile material and DOE spent fuel. To address these problems, this project will investigate the implementation of sensitivity and uncertainty methods within existing Monte Carlo codes used for criticality safety analyses, as well as within a new deterministic code that allows for specification of arbitrary grids to accurately model geometric details required in a criticality safety analysis. A study of the application of sensitivity and uncertainty methodology to relevant EM problems of current interest was conducted. With the help of Michaele Brady Raap at Hanford and Todd Taylor at INEEL, ORNL researchers reviewed applications related to the tank farms and disposal of

spent nuclear fuel to assess the potential changes in safety margin that might be achieved using the sensitivity and uncertainty methodology.

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: Michaele Brady Rapp (Hanford) and Todd Taylor (INEEL)
Collaborating Organization: DOE Nuclear Criticality Safety Program

Description: We have been asked to study the relevance of current critical experiments to validation issues related to implementation of burnup credit in spent fuel safety analyses. Plans call for investigating the use of SEN3, a prototypic computational sequence for obtaining sensitivity and uncertainty (S/U) information for criticality safety applications, to evaluate adequacy of existing critical experiments and reactor critical configurations to validate codes for use in burnup credit in transport casks. SEN3 will be used to model the configurations and casks and the results used to evaluate similarity. Initial analysis of reactor critical configurations and proposed critical experiments have been completed and initial results used to provide NRC with guidance on top priority experiments for use in burnup credit.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborator: R. Y. Lee
Collaborating Organization: United States Nuclear Regulatory Commission

Description: We have been asked to investigate the applicability of a suite of critical experiments planned to support the storage and transport of high-enriched, DOE-EM fuel. The Idaho National Engineering and Environmental Laboratory (INEEL) has significant quantities of highly enriched fresh and spent nuclear fuel in storage. INEEL has proposed to add to the database of critical experiments relative to this application by having critical experiments performed in Russia. Prior to funding such experiments, INEEL has requested that ORNL use the S/U methodology and the SEN3 sequence to evaluate the neutronic similarity of the proposed experiments to the proposed application in transport and storage systems. Evaluations of these experiments have been completed and a draft report has been submitted to the INEEL.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Blair Briggs
Collaborating Organization: INEEL

Materials Science

Project: 55094

Title: Chemical and Ceramic Methods Toward Safe Storage of Actinides Using Monazite

PI: Dr. P. E. D. Morgan *Institution:* Rockwell International Corporation

Description: To investigate the role of radiation damage in altering potential media for the disposition of Pu and other actinides, heavy particle radiation damage experiments were performed, and the damage effects were characterized using TEM, electron diffraction, and other techniques. The experimental

results formed the basis for a new model that can be used to predict wasteform stability in the case of Pu storage.

Collaboration Type: Program interaction *Fiscal Year:* 1997
Collaborator: Prof. R. C. Ewing
Collaborating Organization: Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI

Description: The interaction between electron beams and the rare-earth orthophosphates as manifested by cathodoluminescence were investigated. New information was obtained that can be applied to the analysis of complex ceramics that contain monazite as a constituent phase.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Dr. John M. Hanchar
Collaborating Organization: University of Notre Dame, Department of Civil Engineering and Geological Sciences, Notre Dame, IN. (BES project)

Description: To investigate the role of radiation damage in perovskite and pyrochlore phases that are constituents of titanate (SYNROC)-type ceramics for Pu disposal, techniques for the growth of pyrochlore single crystals were developed, and TEM and RBS studies of radiation effects in perovskites and pyrochlores were carried out. New insight into the radiation resistance of pyrochlore and perovskite phases has been obtained.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Dr. W. J. Weber
Collaborating Organization: Battelle Pacific Northwest Laboratory, Richland, WA. (EMSP Project 54672)

Project: 60118

Title: Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms
PI: Dr. Mark A. Williamson *Institution:* ANL

Description: The end of the Cold War raised the need for the technical community to be concerned with the disposition of excess nuclear weapon material. The plutonium will either be converted into mixed-oxide fuel for use in nuclear reactors or immobilized in glass or ceramic waste forms and placed in a repository. The stability and behavior of plutonium in the ceramic materials as well as the phase behavior and stability of the ceramic material in the environment is not well established. The purpose of this project is to determine the thermodynamic data essential to developing an understanding of the chemistry and phase equilibria of the waste form materials proposed as immobilization matrices. Collaboration with DOE-MD program for Dispositioning of Plutonium by Immobilization.

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborating Organization: DOE-MD

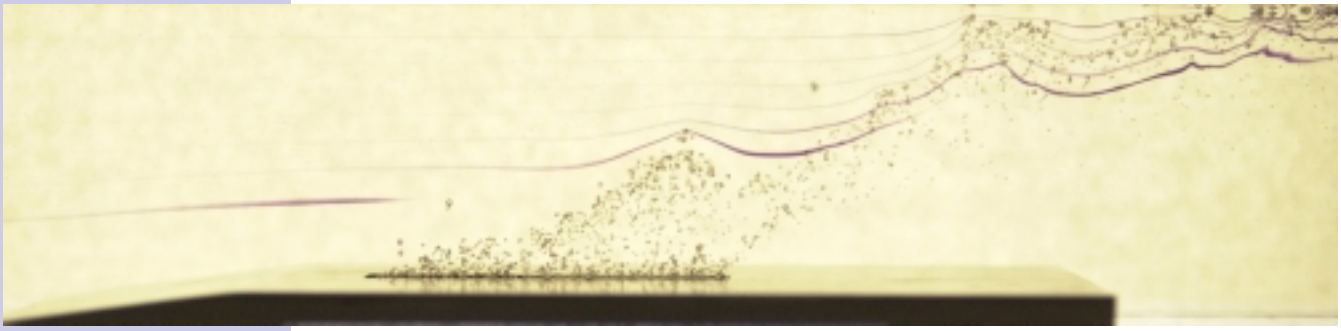
SPENT NUCLEAR FUEL

Engineering Science

Project: 60144

Title: Flow Visualization of Forced and Natural Convection in Internal Cavities
PI: Dr. John C. Crepeau *Institution:* University of Idaho

Description: The INEEL has developed a half-scale experiment to measure fluid dynamic processes in an idealized SNF canister by fabricating a quartz model for use in INEEL's unique large Matched-Index-of Refraction flow system. Currently, two-component laser Doppler velocimetry is used to measure velocity and turbulence components. The present experiment is aimed at examining basic, generic flow processes occurring. Measurements to date emphasize the semi-confined impigning jet and recirculating flow in the region between the perforated basket support plate and the bottom of the canister in a hypothesized approach for drying and passivation. These data should be valuable for assessing and benchmarking computer codes purported to predict flow patterns in SNF canisters during these operations. The status and plans of this project were presented to the National and INEEL SNF Programs at the 2nd EM Science Workshop and further discussions were subsequently held with the National SNF Program staff. An earlier summary was presented to the SNF technical community at the ANS Topical Meeting in Charleston, SC.
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborating Organization: National and INEEL SNF Programs



A fluid containing hexanoic acid reacts with sodium metal embedded in an aluminum plate to produce hydrogen bubbles. The dye illustrates the disturbances in the flow caused by the bubbles. This reaction simulates a passivation reaction during treatment of corroded spent nuclear fuels. [see Project #60144]

Description: The goal of this program is to develop innovative flow visualization methods and predictive techniques for energy, mass and momentum transfer in the presence of chemical reactions in the drying and passivation of spent nuclear fuel (SNF) elements. Efforts on this project are coordinated with the National Spent Nuclear Fuel programs. Their staff have provided guidance on the wide range of SNF canister configurations and fuel elements in use; from this information this EMSP project has developed the descriptions of generic flow processes of concern and, thereby,

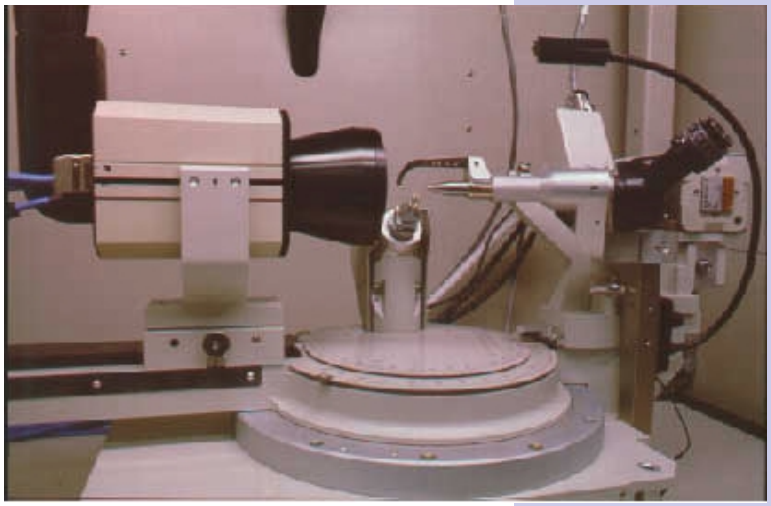
designed the experiments conducted. The SNF staffs have provided understanding of needs for fundamental studies and have reviewed project results and plans for our fundamental studies.

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborating Organization: National Spent Nuclear Fuel programs

Geochemistry

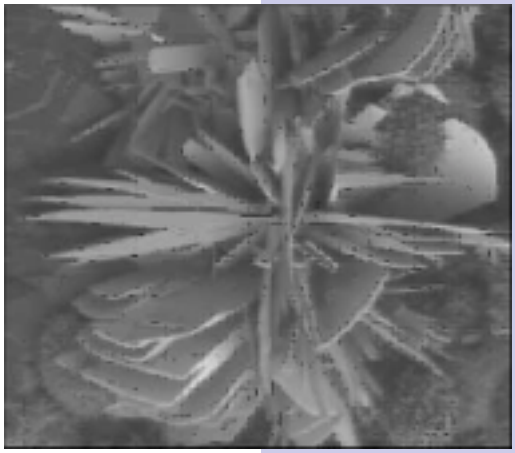
Project: 73691 (Renewal of Project 59960)

Title: Renewal of Direct Investigations of the Immobilization of Radionuclides in the Alteration Products of Spent Nuclear Fuel
PI: Dr. Peter C. Burns
Institution: University of Notre Dame



The CCD-based X-ray diffraction system used to determine the structures of many uranyl phases. [see Project #73691, renewal of #59960]

Description: In an oxidizing environment, such as the proposed repository at Yucca Mountain (YM), rapid alteration rates are expected for spent nuclear fuel. Laboratory-scale simulations demonstrate that the dominant alteration products under YM repository conditions will be uranyl phases. There is an inadequate database to relate the effects of alteration products to the release of radionuclides, although this information is essential for providing realistic radionuclide-release estimates. It is likely that many radionuclides contained in spent fuel will be incorporated into alteration products with a potentially profound impact on the future mobility of radionuclides in the repository. Our objective is to characterize the incorporation of radionuclides into U(VI) alteration products by synthesizing uranyl phases doped with radionuclides, appropriate surrogate elements, or non-radioactive isotopes, followed by detailed phase characterization by diffraction and spectroscopic techniques. This research will permit a more realistic estimate of the release rates of radionuclides from the repository's near-field environment.



An SEM image of a new uranyl silicate phase found growing on actinide-bearing borosilicate wasteglass (S51) from Savanna River. The glass was placed in 100% humidity at 200C for 60 days. This phase is new to science. The crystal structure was determined using X-ray diffraction, and obtained chemical analysis with an electron probe. This phase is potentially a very important sink for actinides where waste forms are altered under repository conditions. [see Project #73691, renewal of #59960]

In collaboration with Rudolph Olson of ANL, we solved the crystal structure of a novel uranyl silicate formed during the corrosion of an actinide-bearing waste glass. The structure contains sheets of eight- and four-membered silicate tetrahedral rings, linked

framework are occupied by low valence cations including K and Na, as well as water molecules. We expect this phase to form under YM repository conditions.

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: Rudolph Olson
Collaborating Organization: ANL

Description: We have been involved in ongoing collaborations with Prof. Rodney Ewing, who has a related EMSP project (73751). Together we have developed prediction mechanisms for the incorporation mechanisms of radionuclides into the uranyl alteration phases that form from spent nuclear fuel.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Prof. Rodney Ewing
Collaborating Organization: University of Michigan

Description: The National Spent Nuclear Fuels Program (NSNFP) is interested in this research concerning the mobility of the radionuclides in Spent Nuclear Fuels (SNF) for their work on the repository at Yucca Mountain. Dr. Burns is collaborating with ANL-E, where they are performing drip tests in a hot cell on commercial SNF. Ms. Davis has a work package funded by the NSNFP which funds ANL-E to perform similar release rate testing on DOE SNF. She is interested in having Dr. Burns perform an analysis on DOE SNF, similar to what he has done on commercial SNF. Dr. Paul Lessing is investigating the incorporation of Gadolinium as a neutron absorber into the DOE SNF packages which will be sent to Yucca Mountain. He would be interested in having Dr. Burns investigate the mobility of Gd in SNF packages.

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborator: Colleen Shelton-Davis
Collaborating Organization: National Spent Nuclear Fuels Program

Description: Fruitful collaborations established with a group of scientists in the Department of Crystallography at St. Petersburg State University in Russia. Much of the work we have done together has been focused on the crystal chemistry of uranyl molybdates, and has already led to several publications. We have studied naturally occuring uranyl molybdates from Russia as a natural analog to phases that may form when spent nuclear fuel is altered under conditions expected in the proposed repository at Yucca Mountain. We have also studied numerous synthetic uranyl molybdates, and are developing a detailed understanding of the crystal chemistry of these complex phases.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Prof. Krivovichev and Prof. Filatov
Collaborating Organization: Department of Crystallography, St. Petersburg State University, Russia

Description: This project has developed a collaboration with Dr. Lynda Soderholm of Argonne National Laboratories concerning the crystal chemistry of actinides. This research is focused on XAS spectra of uranyl minerals and compounds. Ongoing research is being done at the BESRC beamline of the APS.

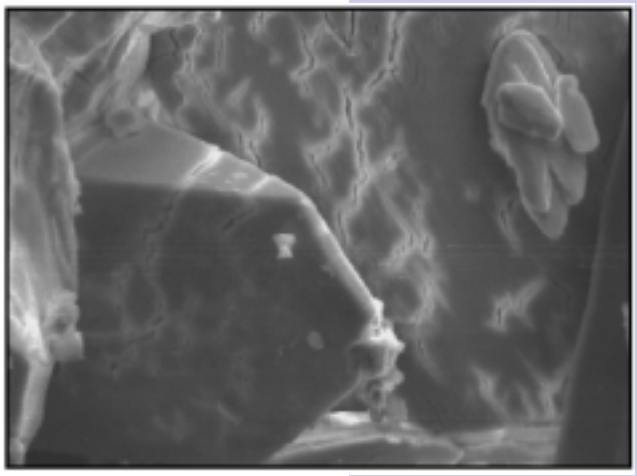
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. Lynda Soderholm
Collaborating Organization: Argonne National Laboratories

Project: 73751 (Renewal of Project 59849)
Title: Corrosion of Spent Nuclear Fuel: The Long Term Assessment
PI: Dr. Rodney C. Ewing *Institution:* University of Michigan

Description: As a result of the work and expertise developed during this EMSP project, the lead principal investigator has been asked to serve on the following panels and committees:

- Invited guest to the Nuclear Waste Technology Review Board
- Invited expert to the Advisory Committee on Nuclear Waste of the NRC
- Member of the Board of Radioactive Waste Management of the National Research Council/National Academy of Sciences

Collaboration Type: Consulting
Fiscal Year: 2001
Collaborator: (See description)
Collaborating Organization: (See description)



SEM-image of a uranyl sulfate hydrate precipitate on johanneite from the Oklo open pit. [see Project #73751, renewal of #59849]

Description: In the area of spent nuclear fuel corrosion, we maintain an active program of collaborations with the following individuals:

Dr. Peter Burns, Notre Dame University
- structural studies and refinements of uranium minerals.

Dr. Jordi Bruno, QuantiSci, Barcelona, Spain
- leaching studies of uranium minerals; solution chemistry of actinides.
- studies on the corrosion of UO2.

Dr. Ignasi Casas, Department of Chemistry, UPC, Barcelona, Spain
- leaching studies of uranium minerals.
- studies on the corrosion of UO2.

Dr. Fanrong Chen, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, P.R. China
- geochemical modeling of uranium-phase dissolution.

Professor Sue Clark, Department of Chemistry Washington State University
- structure-based models of solubility.
- on the incorporation of radionuclides into U(6+) compounds.

Dr. Mostafa Fayek, Center of Isotope Geochemistry, ORNL
- isotopic studies of uranium deposits.

Professor Frank Hawthorne, Department of Geological Sciences, University of Manitoba
- crystal structure refinements of uranium minerals.

Professor Hiroshi Hidaka, Department of Earth And Planetary Systems Science, Hiroshima University
- SIMS analysis of uranium-bearing phases.

Professor Janusz Janeczek, Faculty of Earth Sciences, University of Silesia
- mineralogy and geochemistry of the Oklo reactors.

Professor Takashi Murakami, Mineralogical Institute, Tokyo University
- studies of uranium phases by FEG-TEM and x-ray diffraction analysis.

Dr. Juan de Pablo, Department of Chemical Engineering UPC, Barcelona, Spain
- leaching studies of uranium minerals.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: (see description)
Collaborating Organization: (see description)

Description: The UO2 in spent nuclear fuel is not stable under oxidizing conditions. Under oxic conditions, the U(IV) has a strong tendency to exist as U(VI) in the uranyl molecule, UO22+. The uranyl ions react with a wide variety of inorganic and organic anions to form complexes which are often highly soluble. The result is rather rapid dissolution of UO2 and the formation of a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. The reaction rates for this transformation are rapid, essentially instantaneous on geologic time scales. Over the long term, and depending on the extent to which these phases can incorporate fission products and actinides, these alteration phases become the near-field source term. Based on those guidelines, a survey of the role of colloids in spent fuel corrosion and radionuclide mobility was recently conducted for the National Spent Fuel Program at the INEEL.

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborating Organization: INEEL

Description: Dr Rodney C. Ewing, PI, has been asked to paricipate in the TRW Environmental Division review of the total system performance of the Yucca Mountain Repository and the Nuclear Waste Technology Review Board review of the TSPA of the Yucca Mountain Repository.

Collaboration Type: Consulting *Fiscal Year:* 2000
Collaborating Organization: TRW Environmental Division

SUBSURFACE CONTAMINATION

Actinide (Heavy Element) Chemistry

Project: 70050

Title: Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone

PI: Dr. S. Michael Angel *Institution:* University of South Carolina

Description: DOE requires improved technologies for characterization and monitoring for site clean-up and waste processing applications. Especially needed are field deployable methods and devices for real-time monitoring to reduce dependency on laboratory analyses that are costly and time consuming. Improved sensing capabilities are needed for on-site analyses to provide real-time analytical capabilities for screening level and/or decision-quality data. Matrices of interest to the DOE are soils (or other solids), slurries, and aqueous and non-aqueous solutions. In-situ methods have been demonstrated for identifying high concentrations of organic liquids (e.g., Raman spectroscopy) and low concentrations of a few types of organic molecules (e.g., UV fluorescence and DUVAS), as well as a few selected organic molecules (e.g., sensors) at low concentrations. However, currently there is no method for measuring low levels of organic vapors of the type that would be indicative of subsurface contamination in the vadose zone. The proposed research focuses specifically on a method, resonance-enhanced multi-photon ionization—REMPI, for measuring organic solvents in a soil matrix by detecting organic vapors in the vicinity of a NAPL. We propose using this technique in combination with Raman spectroscopy thus allowing organic contaminants to be measured and identified over a very wide range of concentrations. Our proposed REMPI studies are different from current approaches in that we will use a visible laser for excitation rather than a UV laser, as is used by other groups, to reduce the cost and complexity of the instrumentation, and make the system more robust and reliable. Furthermore, visible wavelengths are more compatible with existing fiber-optic probes and will make it easier to make field measurements using long fiber cables.

LLNL VOC test chamber with achromatic free space focusing. [see Project #70050]

A highly multidisciplinary collaborative group of scientists has been assembled for this project. Angel (analytical chemist with experience with sensors and probe designs), Gribb (civil engineer with expertise in hydraulic measurements, cone penetrometer measurements and soil column design), Colston, Gold, and Brown (expertise in OPO laser measurements,

cone penetrometer instrumentation, and subsurface measurements using fiber optics). Furthermore, experts in cone penetrometer experiments will help in the field studies.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Bill Colston, David M. Gold, and Steve Brown
Collaborating Organization: LLNL

Description: An in-situ field test of a prototype REMPI detection instrument is in the planning stages. Laboratory results indicate ppb detection levels of some VOC's (toluene, benzene, etc.) even within complex mixtures with a simple probe which is compact enough for integration into a cone penetrometer and rugged enough for field testing. The collaboration will utilize experts in cone penetrometry field tests at the SRS (SRS), the technical and fabrication abilities of LLNL, and the analytical chemistry measurements of USC.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Joseph Rossabbi
Collaborating Organization: SRS

Project: 70132 (Renewal of Project 54683)

Title: Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site

PI: Dr. Ken O. Buesseler *Institution:* Woods Hole Oceanographic Institute

Description: High sensitivity thermal ionization mass spectrometry (TIMS) is used to detect the Pu isotopes in all size and redox fractions, thus providing information not only on Pu concentrations but on the Pu source, which can strongly influence Pu speciation and mobility. The combination of these state-of-the-art procedures and the demonstrated care taken to process these samples ensures that the data represent the original in-situ speciation. The results of such a careful basic research program would: i) provide the basis for accurate modeling and prediction of actinide transport; ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/groundwater zone, and iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwaters. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies. Based on this research, our project is collaborating with PNNL utilizing the TIMS facility to study Pu ratios for transport rates. Field sampling is also being done at SRS F basin and Handford 100 K Area to support plume definition and predictive modeling efforts.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborating Organization: PNNL

Project: 70176

Title: Transuranic Interfacial Reaction Studies on Manganese Oxide Hydroxide Mineral Surfaces
PI: Dr. Heino Nitsche
Institution: LBNL

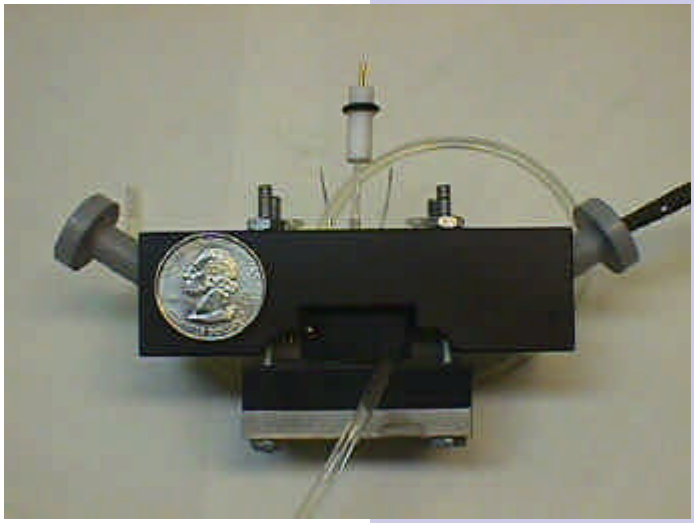
Description: Several DOE sites have been contaminated by transuranic radionuclides (TRU). Manganese oxide/hydroxide minerals, present as minor phases in the vadose zone, can preferentially sequester TRU over iron oxides and other minerals present in much larger quantities. In order to understand the interactions between TRU and manganese oxyhydroxide minerals, we are investigating interfacial reactions between plutonium and manganese based minerals relevant to contaminant transport in the vadose zone. We are currently determining the parameters governing the sorption of aqueous plutonium(VI) ions on well-characterized mineral surfaces as a function of pH, actinide concentration and ionic strength. These investigations will be extended to plutonium(V) and plutonium(IV) as well. In addition to sorption measurements, we are also using x-ray absorption fine structure (XAFS) spectroscopy to determine the local structure and oxidation states of the sorbed plutonium ions.
Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: R. J. Serne
Collaborating Organization: PNNL

Analytical Chemistry & Instrumentation

Project: 70010 (Renewal of Project 54674)

Title: Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone
PI: Dr. William R. Heineman *Institution:* University of Cincinnati

Description: A proposed new sensor concept combines the elements of electrochemistry, spectroscopy, and selective partitioning into a single device that provides three levels of selectivity. This type of sensor has many potential applications at DOE sites. As an example, the enhanced specificity embodied in this new sensor design is well-suited to the analytical problem posed by the addition of ferrocyanide to radioactive tank wastes at the DOE-Hanford Site. A demonstration of a sensor package (mircocell and instrumentation) was performed on the waste tank sample.
Collaboration Type: Program interaction
Fiscal Year: 2000
Collaborator: Dr. Heineman - University of Cincinnati
Collaborating Organization: Hanford Site



Prototype sensor can accommodate a sample volume of 800 mL. Working electrode consists of an indium tin oxide slide coated with a charge selective film; the blue LED provides a simple light source. [see Project #70010, renewal of #54674]

Project: 70179

Title: Radionuclide Sensors for Water Monitoring
PI: Dr. Jay W. Grate *Institution:* PNNL

Description: Our research program is directed toward developing novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. In order to meet the requirements for isotope specific detection at ultra-low regulatory levels the proposed sensors are based on radiometric detection. In order to address the fundamental challenge of short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector, using automated microfluidics for sample manipulation and sensor regeneration or renewal. Radionuclides of primary interest for DOE needs are Sr-90, Tc-99, and actinides. Jim Roane a Ph.D. student from Clemson who is involved in work on this EMSP program, worked with Drs. John Leyba and Raymond Sigg at the SRS evaluating the TEVA and ABEC extractive scintillator materials for potential application of on-line process monitoring for Tc.
Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: SRS

Description: We have established collaboration with the University of Arkansas at Little Rock (Professor Malay Mazumder, Department of Applied Sciences) on the synthesis and production of dual functionality scintillator/sorbent materials for radionuclide sensing. Dr. Mazumder will explore electrostatic microencapsulation methods to produce materials with required properties.
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. Malay Mazumder
Collaborating Organization: University of Arkansas at Little Rock

Biogeochemistry

Project: 55388

Title: Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents
PI: Dr. Neil C. Sturchio *Institution:* ANL

Description: The purpose of this project was to investigate the potential applications of stable isotope ratio measurements in characterization of the source terms, the transport, and the fate of chlorinated solvents in groundwater aquifers. The approach to this research was threefold: to develop methods for the sampling and isotopic analysis of chlorinated solvents in groundwaters; to perform laboratory experiments to measure equilibrium and kinetic isotope effects associated with biological and physical transformation processes of chlorinated solvents; and to perform field investigations at well-characterized, contaminated aquifer sites to demonstrate the applicability of the isotopic approach in real-world situations. To further these means the following collaborations were established:

- Mr. Jay Clausen (Lockheed-Martin Energy Systems, Inc., Kevil, KY (now at Ogden Energy and Environmental Systems, Inc., Westport, MA), on application of chlorine isotope ratio measurements in an investigation of natural attenuation of trichloroethene at the Paducah Gaseous Diffusion Plant.

- Mr. Greg Smith, ENSR, Inc. (now at Radian International), on application of carbon and chlorine isotopic measurements to solvent cleanup activities at a number of industrial sites.

- Dr. Chris Reddy, Woods Hole Oceanographic Institute, Woods Hole, MA, on application of chlorine isotope measurements to environmental studies of semivolatile chlorinated organics (e.g., PCBs and pesticides).

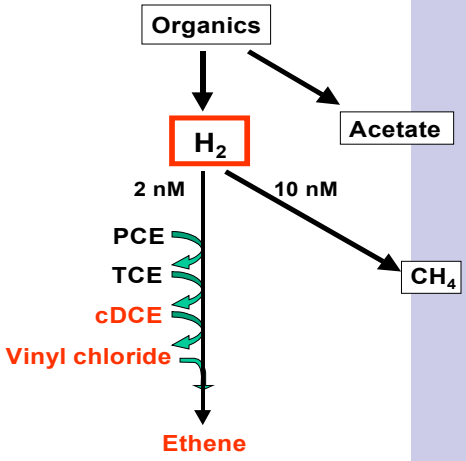
Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborator: (see description)
Collaborating Organization: (see description)

Project: 70063 (Renewal of Project 54666)

Title: Biodegradation of Chlorinated Solvents: Reactions Near DNAPL and Enzyme Function
PI: Dr. Perry L. McCarty
Institution: Stanford University

Description: The effects of radiation from the decay of radionuclides in nuclear waste and other nuclear materials may potentially impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. Using experimental and computer simulation approaches, this project endeavors to develop the underpinning science and models necessary to assess the effects of radiation on the performance of glasses and ceramics designed for the immobilization of high-level tank waste and stabilized nuclear materials. Collaborations with PNNL and LANL have been developed to help further these objectives.

Collaboration Type: Program interaction
Fiscal Year: 2000
Collaborator: N.J. Hess, B.D. Begg, L.R. Corrales, H.L. Heinisch, and R.E. Williford; S.D. Conradson
Collaborating Organization: PNNL; LANL



PCE (or TCE) is stepwise reductively dehalogenated to the less chlorinated ethenes cDCE and VC. Concentration values indicate the hydrogen threshold concentration below which a pathway (dehalogenation or methanogenesis) usually does not operate. [see Project #70063, renewal of #54666]

Project: 70165

Title: Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation

PI: Dr. Fred J. Brockman *Institution:* PNNL

Description: In situ bioremediation of contaminants can offer advantages in cost, speed, public acceptance, and final cleanup levels achieved relative to physical removal methods. However, the lack of knowledge on how physical and hydrologic features of the vadose zone control the spatial distribution of microbial biotransformation activity and the potential for microorganisms to colonize this region raises questions about the feasibility of deep vadose zone bioremediation, and causes very large uncertainties in the accuracy of current model predictions. Because of the PI's understanding biological processes and bioremediation in the vadose zone, he has been asked by INEEL to write the biological transformation processes portion of the Vadose Zone Complex Wide Science Needs and Capabilities document.

Collaboration Type: Consulting *Fiscal Year:* 2000

Collaborating Organization: INEEL

Project: 73784 (Renewal of Project 55267)

Title: Microbially Mediated Immobiliuzation of Contaminants Through In Situ Biostimulation: Scale up of EMSP project 55267

PI: Dr. Philip M. Jardine *Institution:* ORNL

Description: The purpose of this research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that subsurface microbial activity can effectively alter the redox state of toxic metals and radionuclides so that they are immobilized for long time periods. The overall goal of this project is to use basic research to develop a cost effective remediation strategy that employs in situ contaminant immobilization. Specifically, we will develop active biowall technologies to contain priority EM contaminant plumes in groundwater. Interaction with several other EMSP projects with regard to technology transfer, data sharing, and collaboration on experimental designs.

Experiments by an EMSP project are designed to help determine optimum operating conditions for hydrothermal oxidation of aqueous mixed wastes. In this photo, scientists load uranium (VI) oxide samples into a rocking autoclave for solubility measurements at high temperatures. [see Project #73784, renewal of #55267]

Collaboration Type: Program interaction

Fiscal Year: 2000

Collaborator: Dr. Eric Roden (EMSP Project 55164) and Dr. Lenly Weathers (EMSP Project 55071)

Collaborating Organization: University of Alabama and Tennessee Technological University

Engineering Science

Project: 70088

Title: Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

PI: Dr. Baolin Deng *Institution:* New Mexico Institute of Mining & Technology

Description: Immobilization of toxic and radioactive metals (e. g., Cr, Tc, U) in the vadose zone by in situ gaseous reduction (ISGR) using hydrogen sulfide (H2S) is a promising technology being developed by the U. S. Department of Energy (DOE) for soil remediation. Earlier laboratory studies at the PNNL (PNNL) have shown that Cr(VI) in a number of soil samples can be effectively immobilized by treatment with diluted H2S. A field test has also been completed which resulted in 70% immobilization of Cr(VI). The objective of this collaborative project between PNNL and New Mexico Tech is to seek basic scientific understanding concerning the kinetics and mechanisms of interactions among H2S, the metal contaminants, and soil components.

Collaboration Type: Joint interaction *Fiscal Year:* 2001

Collaborating Organization: PNNL

Project: 73793 (Renewal of Project 55013)

Title: Biofiltration of Volatile Pollutants: Solubility Effects

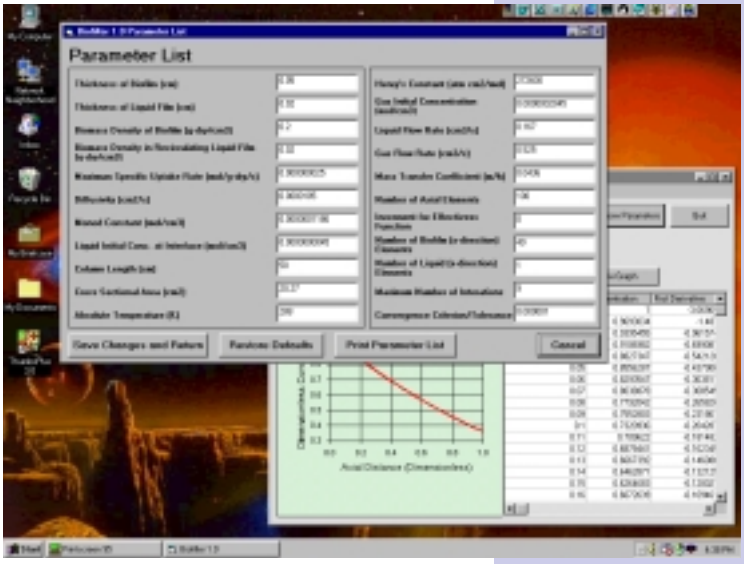
PI: Dr. Brian H. Davison *Institution:* ORNL

Description: This work seeks to produce industrial and EM-relevant scientific information for successful biofiltration operation with a continued emphasis on in situ, discussion of current TCE treatment by air stripping, and biological degradation using methane at SRS. A discussion regarding how better data and modeling tools could help select remediation approaches was held. The difficulty of bringing fundamental research to deployment, end-user, and focus group needs has also been examined. SRS has indicated it is willing to be a new test site for new approaches including biofiltration - if further funding can be secured.

Collaboration Type: Program interaction

Fiscal Year: 1998

Collaborating Organization: SRS



Biofilter design software was developed for Windows 95/98™ to enable users to quickly and easily determine how various operating parameters will impact their biofilter designs a priori. The user interface is straightforward; data may be copied and then pasted into spreadsheets or presentation packages. Calculation times vary from ~5 seconds to ~5 minutes on Pentium™-class processors. [see Project #73793, renewal of #55013]

Description: Biofilter design software was developed for Windows 95/98TM to enable users to quickly and easily determine how various operating parameters will impact their biofilter designs a priori. The user interface is straightforward; data may be copied and then pasted into spreadsheets or presentation packages. We have provided beta-program for operational predictive biofilter to University of California Riverside. ORNL completed further development of a comprehensive two-dimensional predictive model to elucidate mass transfer and kinetic limitations in these systems. This model can be extended to a variety of columnar biofiltration systems by changing appropriate parameters.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborating Organization: University of California Riverside

Geochemistry

Project: 54741

Title: Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria
PI: Dr. Michael T. Murrell *Institution:* LANL

Description: Consulted regarding uranium measurements at Rocky Flats by contractors for Rocky Flats and the State of Colorado. We later received a small amount of funding to make some measurements for solar pond waters at Rocky Flats. The approach used was similar to that of our EMSP project.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dave Janecky
Collaborating Organization: Rocky Flats Environmental Technology Site, State of Colorado

Project: 70070

Title: Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks
PI: Dr. Kathryn L. Nagy *Institution:* University of Colorado

Description: Since the late 1950s, leaks from 67 single-shell tanks at the Hanford Site have been detected or suspected, resulting in the release of about 1 million curies to the underlying sediments. The Hanford Tri-Party Agreement calls for the initiation of remediation at the 200 Area tank farms in 2004. There is a risk that these activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone. At issue is the distribution of contaminants beneath the tanks, the processes that led to their current disposition, and the processes that will control their future mobility. The high ionic strength, high pH, and high aluminum concentrations in the tank liquids can significantly alter the vadose zone sediments through dissolution of primary minerals and precipitation of secondary minerals. Data obtained will be directly useful to other EMSP projects addressing contaminant mobility in the vadose zone. The ILAW project and Vadose Zone Characterization project, both run by CH2M-Hill Hanford Group (CHG)

at Hanford, are using the lab data on the caustic attack on Hanford sediments to augment similar work that is being performed under direct funding from them. We have also shared the information, samples of Hanford sediment, and recipes for simulated Hanford tank wastes with several other EMSP investigators. Similar interactions are ongoing with other scientists funded by the S&T integration project [Dave Bish and Peter Lichtner at LANL, Carl Steefel and Susan Carroll at LLNL].

Collaboration Type: Program interaction *Fiscal Year:* 2001

Collaborator: Jiamin Wan, Markus Flury, Jon Chorover, Dave Bish and Peter Lichtner, Carl Steefel and Susan Carroll

Collaborating Organization: LBL, WSU-Pulllman, Penn State, LLNL, LANL

Project: 70081

Title: Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases

PI: Dr. Samuel J. Traina *Institution:* Ohio State University

Description: Staff on this project have made significant written contributions to the draft WMA S-SX Tank Farm report due March 31, 2001. These contributions have been in conjunction with the Hanford Science and Technology project (River Protection Program's Hanford Vadose Zone/Groundwater Integration project).

Collaboration Type: Consulting *Fiscal Year:* 2001

Collaborating Organization: Hanford River Protection Program

Project: 70146

Title: Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in Soils and Vadose Zone Sediments

PI: Dr. Richard J. Reeder *Institution:* State University of New York at Stony Brook

Description: Collaborations are ongoing with two DOE facilities — National Syncroton Light Source at BNL and the Advanced Neutron Source at ANL — to support carbonate mineral characterization and contaminant uptake. Separate co-precipitation experiments with target contaminants will allow an assessment of the effectiveness of uptake during crystallization of calcite, which is favored in the soil and vadose zone as a result of periodic wetting and drying, and also in response to the highly alkaline waste fluids. XAFS spectroscopy will be used to confirm speciation.

Collaboration Type: Joint interaction *Fiscal Year:* 2001

Collaborating Organization: National Syncroton Light Source at BNL and the Advanced Neutron Source at ANL

Description: Lanthanides are useful analogs for the behavior of trivalent actinides. Lanthanides are known to sorb strongly onto calcite and partition coefficients, for coprecipitation of trivalent lanthanides with calcite are very large. Hence, calcite may be a very effective sorbent for trivalent actinide species. However, the uptake of trivalent species poses issues of charge

balance and coordination in the Ca site in calcite. We have formed a collaboration with University of Central Florida physicist Dr. Robert Peale and graduate student Sandra Withers to characterize the sites in calcite occupied by lanthanides. High-resolution IR spectroscopy will be used in combination with XAFS spectroscopy to determine the number and type of sites. This information will provide the basis for assessing the long-term sequestration of lanthanides and actinides in calcite.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. R. E. Peale
Collaborating Organization: University of Central Florida

Description: The overall goals of this project are to determine the role of carbonate minerals in the uptake and long-term sequestration of metal contaminant species, with a focus on soil and vadose zone environments. The metal contaminants studied are relevant to radionuclide waste sources at the Hanford Site, as well as other locations throughout the DOE Complex. One aspect of this research involves determination of the molecular-scale interactions of uranium(VI) species with calcium carbonate minerals. This has implications for sequestration of uranyl species with authigenic calcite via coprecipitation, and the finding may influence uranium remediation techniques that rely on carbonate/bicarbonate leaching. The Principal Investigators have collaborated with LANL researchers C. D. Tait and D. E. Morris using luminescence spectroscopy to identify uranyl species coprecipitated with calcite and aragonite. Luminescence spectra have shown that changes in uranyl coordination occurring during coprecipitation may inhibit uptake by calcite. Luminescence data will be combined with XAFS spectroscopy to assess the molecular coordination of uranyl coprecipitated with calcite. This information will be useful for predicting the long-term retention of uranium(VI) by calcite.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. C. D. Tait and Dr. D. E. Morris
Collaborating Organization: LANL

Project: 70163

Title: The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface
PI: Dr. Andrew R. Felmy *Institution:* PNNL

Description: The presence of a wide range of radionuclides, metal ions, inorganic ligands, and organic chelating agents combined with the high base and electrolyte concentration in the Hanford waste tanks creates some unique and difficult problems in modeling the aqueous thermodynamics of these solutions. Solving these problems is important since this can lead to better strategies for tank processing and predictions of subsurface transport. In addition, a large number of scientists and engineers at Hanford and other sites rely on these models for making accurate predictions of tank chemistry. Work is currently being accomplished with the assistance of OLI Systems Inc. to include the Pitzer equations into the ESP tank processing

model. ESP is used by all site contractors for simulating tank sludge washing, salt cake dissolution, etc. The inclusion of the Pitzer equations will allow all of the thermodynamic data generated under the EMSP program to be used by these sites.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborating Organization: OLI Systems Inc.

Geophysics

Project: 70052

Title: Material Property Estimation for Direct Detection of DNAPL Using Integrated Ground-Penetrating Radar Velocity, Imaging, and Attribute Analysis
PI: Dr. John Bradford *Institution:* University of Wyoming

Description: Many DNAPLs, including chlorinated solvents, have much lower dielectric permittivity and conductivity than water. A contrast in electric properties is induced when DNAPL displaces water in the sediment column resulting in an anomalous GPR signature. The focus of our work is direct detection of DNAPLs, specifically chlorinated solvents, via material property estimation from surface ground-penetrating radar (GPR) data. To directly identify zones of DNAPL contamination, we focus on three aspects of reflected wave behavior - propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Velocity analysis provides a direct estimate of dielectric permittivity, attenuation analysis is used to identify variations in conductivity, and AVO behavior is used to estimate the dielectric permittivity ratio at a reflecting boundary. Areas of anomalously low dielectric permittivity and low conductivity are identified as potential DNAPL source zones. We are working with personnel at the Savannah River and Hanford sites to identify contaminated field areas for both controlled experiments and exploratory investigation.

Multi-offset, ground-penetrating radar data acquisition for DNAPL detection at the SRS. [see Project #70052]

Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborating Organization: Savannah River Technology Center, Hanford Groundwater/Vadose Zone Integration Project

Project: 70108 (Renewal of Project 55411)

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

PI: Dr. Patricia A. Berge *Institution:* LLNL

Description: We are networking with other current and former EMSP project PI's to plan possible future collaborations on field experiments to test the lab and theory results of this EMSP project, since this EMSP project is developing methods for improving interpretation of field experiment data used for subsurface imaging. The PI for this project provided advice about geophysical field experiment design for subsurface imaging at the Hanford site, at the Advanced Vadose Zone Characterization Workshop, and in follow-up discussions.

Collaboration Type: Joint interaction *Fiscal Year:* 2000

Collaborator: C. Carrigan, E. Majer, D. Steeples, R.J. Knight,

Collaborating Organization: LLNL, LBL, University of Kansas, Stanford/University of British Columbia

Description: The PI for this project was a participant in the Non-invasive Characterization Work Group for the DOE Complex-Wide Vadose Zone Science and Technology Roadmap for Characterization, Modeling, and Simulation of Subsurface Contaminant Fate and Transport. Insights gained in this project and resulting advancements in the area of petrophysics (relating geophysical measurements to hydrological properties and soil composition) have been included in current drafts of the roadmapping report in sections describing the current state-of-the-art of petrophysical relationships.

Collaboration Type: Consulting *Fiscal Year:* 2000

Collaborating Organization: Department of Energy

Project: 70220

Title: High Frequency Electromagnetic Impedance Imaging for Vadose Zone and Groundwater Characterization

PI: Dr. Gregory A. Newman *Institution:* Sandia National Laboratories

Description: In a collaborative effort, geophysicists from Sandia National Laboratories and the Institute of Geophysics and Meteorology at the University of Cologne in Germany have utilized the world's fastest supercomputer, Ascii-Red, at Sandia to produce the first ever 3D tomograpic reconstruction of a hazardous waste site, near Cologne. This breakthrough allows for high resolution 3D images of the subsurface electrical conductivity/ resistivity using radio waves, and provides a new and important diagnostic tool in accessing the risk such sites pose to groundwater and the environment. To produce the 3D images, significant computer resources were required in the processing of the data. These were obtained through the use of massively parallel computers. With these machines, hundreds to thousands of processors are simultaneously employed in the data processing needed for realistic processing times. The fastest versions of these machines are capable of more than a trillion (1,000,000,000,000) floating point operations per second.

The measurement technique used in the reconstructions is known as the radio magnetotelluric method (RMT), where the data arise from radio transmitters, operating between the 500 kHz to 20 kHz frequency band. With funding provided by the German National Science Foundation, the Institute has been a pioneer in the development of the method and its application to hazardous waste site characterization in Germany and the European Community, but has been limited in its capability to image the data in three-dimensions, required for high quality risk assessment. While scientists from Sandia have developed such 3D imaging algorithms under the Environmental Management Science Program (EMSP), they have had limited access to high quality field data sets necessary to verify the accuracy and robustness of these imaging schemes. By joint collaboration between the Institute and the laboratories, an important breakthrough has been achieved.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborating Organization: Institute of Geophysics and Meteorology at the University of Cologne, Germany

Health/Risk

Project: 55033

Title: Characterization of Chemically Modified Hyperthermophilic Enzymes for Chemical Syntheses and Bioremediation Reactions
PI: Dr. Brian H. Davison *Institution:* ORNL

Description: We have discussed our research and their research with Brian Clark of Enzyme Technologies. They have a crude enzyme solution for oxidative attack of organics. We received a sample of their enzyme solution in February 2000 and hope to run a few preliminary tests.
Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Brian Clark
Collaborating Organization: Enzyme Technologies

Description: Research developments in the area of biocatalysis in organic solvents are expected to greatly expand the role of bioprocessing in chemical synthesis, fuel processing, and bioremediation technologies. Many biological transformation reactions of interest to DOE site remediation involve species that are only sparingly soluble in aqueous environments. Hence, destruction of these incalcitrant and toxic materials would benefit tremendously if their degradation could be performed in nonaqueous environments. Organic biocatalysis may be motivated by the nature of the substrate itself, or by augmented mass transport, ease of product recovery, or novel reaction pathways afforded by the organic solvent. For instance, polychlorinated biphenyls (PCB's), dense nonaqueous phase liquids (DNAPL's), and manufactured gas plant wastes are sparingly soluble in water, but may be more effectively processed when solubilized by organic liquids. However, naturally occurring enzymes are not soluble in organic solvents, indeed, most spontaneously denature and, depending on the solvent used, typically form inactive and insoluble precipitates.

Additionally, the identification that PCB degradation is a critical experiment has been made. The diffculty, however, of bridging fundamental research to deployment, end-user, and focus group needs still exists.

Collaboration Type: Program interaction *Fiscal Year:* 1998
Collaborating Organization: SRS

Description: The objective of the proposed work is to gain a fundamental understanding of the molecular and catalytic properties of enzymes that have been chemically modified so that they are soluble and catalytically active in pure organic solvents. Hydrogenases and redox proteins obtained from hyperthermophiles, which are organisms that grow near and above 100°C, will be investigated as model systems, and the lessons learned will be applied to other hyperthermophilic enzymes with bioremediation potential. The premise for this study is that thermostable enzymes which are both soluble and catalytically active in both water and in a range of organic solvents are optimally suited for bioremediation where substrates of interest are more soluble and may be processed with greater specificity in nonaqueous solvents. Recently, a discussion was held with Brian Clark of Enzyme Technologies. He indicated that their facility has a crude enzyme solution for oxidative attack of organics. Working together, a few preliminary tests have been run on this solution.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Brian Clark
Collaborating Organization: Enzyme Technologies

Hydrogeology

Project: 55036

Title: Colloid Transport and Retention in Fractured Deposits
PI: Dr. John F. McCarthy *Institution:* ORNL

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

Fundamental Description Of Particle Transport In Fracture
- Dr. David Walker, Cardiff University, United Kingdom

Colloid Transport In Intact Geological Columns
- Dr. Larry D. McKay, University of Tennessee

Field-Scale Colloid Tracer Migration
- Dr. William E. Sanford, Colorado State University
- Ms. Paige L. Stafford, University of Tennessee

Fracture Network Models of Colloid Transport
- Dr. Motomu Ibaraki, Ohio State University

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: (see description)
Collaborating Organization: (see description)

Project: 55216

Title: In-Situ Characterization of Dense Non-Aqueous Phase Liquids Using Partioning Tracers
PI: Dr. Gary A. Pope *Institution:* University of Texas at Austin
Description: We have developed a new analytic approach that has several advantages over existing approaches for inversion of tracer data. First, the technique utilizes an extremely efficient three-dimensional multiphase streamline simulator as a forward model. Second, the parameter sensitivities are formulated in terms of one-dimensional integrals of analytic functions along the streamlines. Thus, the computation of sensitivities for all model parameters requires only a single simulation to construct the velocity field and generate the streamlines. The methods developed in this project were tested on field data from a saturated Partioning Interwell Tracer Test performed at Hill Air Force Base in Utah and an unsaturated Partioning Interwell Tracer Test performed at Kirtland Air Force Base in New Mexico. The Kirtland test was performed to evaluate a radio frequency enhanced soil vapor extraction remediation technology. The remediation effort was a project of the Advanced Applied Technology Demonstration Facility.
Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: Hill Air Force Base in Utah and Kirtland Air Force Base in New Mexico

Project: 60069

Title: Least-Cost Groundwater Remediation Design Using Uncertain Hydrogeological Information
PI: Dr. George F. Pinder *Institution:* University of Vermont

Description: The project seeks to examine the importance of uncertainty in hydraulic conductivity in the least-cost design of groundwater contamination containment systems. The project uses a new conceptual approach to accommodate aquifer parameter uncertainty in optimal groundwater remediation design and introduces a new operations-research technique to solve the optimization problem. The new approach, Robust Optimization, allows for the determination of a robust, lowest-possible cost, pumping design that is consistent with the inherent uncertainty in the hydraulic conductivity field. It also allows for the visualization of how one can trade off excess pumping for enhanced security. Collaborated with BNL for a review of Brookhaven groundwater contamination.
Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborating Organization: BNL

Project: 70135

Title: Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

PI: Dr. Markus Flury *Institution:* Washington State University

Description: This project seeks to improve the basic understanding of colloid and colloid-facilitated transport of contaminants in the vadose zone. The objectives are to determine the structure, composition, and surface charge characteristics of colloidal particles formed under conditions similar to those occurring during leakage of waste typical of Hanford tank supernatants, to characterize the mutual interactions between colloids, contaminant, and soil matrix, to evaluate mobility of colloids through soil under different degrees of water saturation and solution chemistry, and to determine the potential of colloids to act as carriers to transport the contaminant through the vadose zone. We are currently in the process of establishing collaboration with other groups working on colloid transport at DOE sites. This interaction includes coordination of research activities and providing colloidal material for testing purposes, and characterization of colloidal materials.

Collaboration Type: Program interaction *Fiscal Year:* 2000

Collaborator: John McCarthy and John Selker

Collaborating Organization: ORNL and Oregon State University

Project: 70149 (Renewal of Project 54950)

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

PI: Dr. Charles R. Carrigan *Institution:* LLNL

Description: Many releases of chemical solvents or DNAPLS occur at the surface causing the vadose layer to be the first part of a hydrologic system to interact with the contaminant. As the entry point of these chemicals into a groundwater system, the vadose zone can become a long-term source function for contamination that is metered by natural processes into the underlying saturated zone for further dispersal. However, a contaminant plume does not remain unaffected by the surrounding unsaturated soil. Heterogeneous vadose regimes, such as those containing fractures or other permeability heterogeneities, are the sites of complex interactions between the atmosphere and groundwater. When a volatile contaminant exists as free product or in dissolved form in the vadose environment, upward transport can occur with the contaminant ultimately being vented as a vapor into the atmosphere. It is known that partitioning of a liquid contaminant into the vapor phase can be a very effective means of decontamination. The subsequent

Electric Resistance Tomography (ERT) monitoring capability at the Vadose Zone Observatory (VZO). [see Project #70149, renewal of #54950]

transport of the vapor occurs naturally and can be enhanced, for example, by the anisotropy resulting from fractured-matrix-flow paths as well as by certain heterogeneity distributions. Several stages in the transport process are involved in going from a volatile, liquid state contaminant to a contaminant vapor vented at the surface. In a three-year effort, we will investigate the detailed nature of each of these stages of transport in the vadose zones of fractured and heterogeneous regimes with the (1) aid of existing data, (2) new field studies involving dissolved tracer gases and (3) 3-D diagnostic computer simulations that provide a framework to interpret our observations. We will emphasize determining the impact of features specific to a site, that is, the local geology and hydrology, on each stage of the transport process. In particular we want to better understand how the time scales for (1) partitioning contaminants from the liquid to the vapor states and then (2) transporting the vapor out of the vadose regime are dependent on the specific character of a site. Such time-scale information will be important for determining the appropriate response to vadose zone contamination including the option of natural remediation, that is, no response. This information can also be interpreted as a baseline performance criterion for proposed soil-venting schemes. Not least, this work will result in the development of new field methods, involving the injection and analysis of dissolved rare-isotope and chemical-compound tracers, that we anticipate applying to sites at Lawrence Livermore and to the thick, fractured basalt vadose regime at the Idaho National Engineering Laboratory. As such, another (EMSP-EMSP) collaboration based on this philosophy has been completed with Boris Faybishenko at LBNL involving the development of a combined tensiometer/lysimeter system that was developed for use at the VZO.

Researchers with the new Electromagnetic Induction Tomography (EMIT) tool, designed for subsurface characterization of a contaminated site. [see Project #70149, renewal of #54950]

The VZO site during the infiltration experiment and EMIT tool test. [see Project #70149, renewal of #54950]

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Boris Faybishenko
Collaborating Organization: LBNL

Description: In August 2000, we hosted Ernie Majers and Ken Williams (EMSP-EMSP) of LBNL for a test of their cross borehole radar system. The VZO afforded a comparision between a portable in-hole imaging system (radar) and the permanently installed ERT system at the VZO.
Collaboration Type: Program interaction
Fiscal Year: 2000
Collaborator: Ernie Majers/ Ken Williams
Collaborating Organization: LBNL

Description: Collaboration with the Defense Nuclear Facilities Safety Board (DNFSB) is currently ongoing by working with their doctoral and post-doctoral researchers to enhance vadose zone transport and predictive modeling expertise. A stated need of the DOE EM program is a better understanding of basic vadose zone fluid flow and contaminant transport processes for the purpose of making improved estimates of contaminant release rates and fluxes across the vadose zone to the water table at DOE sites such as the tank farms at Hanford.
Collaboration Type: Joint interaction
Fiscal Year: 2001
Collaborating Organization: Defense Nuclear Facilities Safety Board

Description: The VZO has become an official testbed for the National Science Foundation sponsored Center for Subsurface Sensing and Imaging Systems (CenSSIS). The Principal Investigator (C.R. Carrigan) has served as consultant to the CenSSIS program. In November 2000, he gave an invited presentation at the First Industrial Collaboration Conference because of his work with the VZO. CenSSIS is an NSF Engineering Research Center dedicated to developing techniques to image and explore subsurface regimes. You can learn more about CenSSIS at http://www.censsis.neu.edu/. The invited presentation is available by clicking on the flashing link "Nov 13-15 Presentations" on the main CenSSIS webpage.
Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: Center for Subsurface Sensing and Imaging Systems (CenSSIS)

Description: As a result of CenSSIS, two collaborations are being developed. One involves a proposal on subsurface sensing and data telemetry with Electrical Engineering Professor Qing H. Liu at Duke University, while the other concerns the use of Electric Impedance Tomography (EIT) at the VZO. EIT was developed and refined originally for medical applications by Prof. David Isaacson at Renssaleer Polytechnic Institute and others. Our joint effort will seek to incorporate some of the refinements developed for medical purposes into EM problems involving imaging of contaminant plumes at at the VZO.
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Prof. Qing H. Liu/ Prof. David Isaacson
Collaborating Organization: Duke University/ Renssaleer Polytechnic Institute

Description: GeoSystems Analysis, Inc., Tucson, Az is using subsurface barometric pressure fluctuations obtained from the Vadose Zone Observatory monitoring wells and stored in a monitoring database to use in his model for estimating subsurface soil permeabilities.
Collaboration Type: Consulting
Fiscal Year: 2000
Collaborator: Jim Lombard
Collaborating Organization: GeoSystems Analysis, Inc.

Description: In September 2000, we carried out a joint experiment at the VZO with researchers from Electromagnetic Instruments (EMI) in Emeryville, CA., Techniscan Inc. in Salt Lake City, Utah, and observers representing SBIR contracts involving Tyndall Air Force Base. The purpose of the collaboration was to test a new Electromagnetic Induction Tomography (EMIT) tool that was designed for subsurface characterization of a contaminated site. The new portable, borehole tool was compared with an existing Electric Resistance Tomography (ERT) system permanently installed at the site. We found that this new device exhibited sensitivity to electrical conductivity changes resulting from plume migration that is comparable to our ERT system. This first test of the borehole EMIT tool was a positive result that is potentially significant for future subsurface characterization studies at contaminated DOE sites.
Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: Electromagnetic Instruments (EMI) in Emeryville, CA./ Techniscan Inc. in Salt Lake City/Tyndall Air Force Base

Project: 70193

Title: Influence of Clastic Dikes on Vertical Migration of Contaminants in the Vadose Zone at Hanford
PI: Dr. Christopher J. Murray *Institution:* PNNL

Description: Our project has developed a collaboration with the Science and Technology Effort of the Groundwater/Vadose Zone Integration Project at the Hanford Site. The Groundwater/Vadose Zone Integration Project recently paid the costs of excavating a clastic dike that we were preparing to study. Scientists working with the Groundwater/Vadose Zone Integration Project are also performing drip infiltration tests on the clastic dike and matrix sediments exposed by the excavation. This collaborative research will provide data that will support our EMSP project, as well as the needs of the Hanford Groundwater/Vadose Zone Integration Project.
Collaboration Type: Joint interaction *Fiscal Year:* 2000
Collaborating Organization: Groundwater/Vadose Zone Integration Project at the Hanford Site

Project: 70219

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

PI: Dr. Philip M. Jardine *Institution:* ORNL

Description: Philip M. Jardine, PI, is conducting a related project for OBER. Where practical and beneficial, research activities are dovetailed. Technology/research transfer between the two projects achieves more for each at less cost and on an accelerated schedule because they are strongly linked. Their joint research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for tank farm restoration.

Collaboration Type: Joint interaction *Fiscal Year:* 2001

Collaborator: Dr. Philip M. Jardine

Collaborating Organization: DOE Office of Biological and Environmental Research project, Influence of Coupled Processes on the Fate and Transport of Industrial Mixed Waste Plumes in Structured Media

Description: The two projects are resolving the same issues related to the fate and transport of radionuclides beneath the Hanford tank farms. The projects differ only in the type of radionuclides used and the type of geologic formation used. The research projects are strongly linked and will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for tank farm restoration. Technology/research transfer between the two projects will be beneficial to both.

Collaboration Type: Joint interaction *Fiscal Year:* 2001

Collaborator: Dr. Philip M. Jardine and Dr. John M. Zachara

Collaborating Organization: PNNL EM project Geochemical and Hydrological Processes Influencing the Fate and Transport of 90Sr Beneath the Hanford Tank Farms

Description: The two projects are working with the same type of media. Where practical and beneficial, research activities are dovetailed. When media samples were collected for this project at Hanford, samples were also collected for Dr. Tokunaga's project, saving time and money. Technology/research transfer between the two projects will be beneficial to both.

Collaboration Type: Joint interaction *Fiscal Year:* 2001

Collaborator: Dr. Tetsu K. Tokunaga

Collaborating Organization: EMSP project #70069, Fast Flow in Unsaturated Coarse Sediments

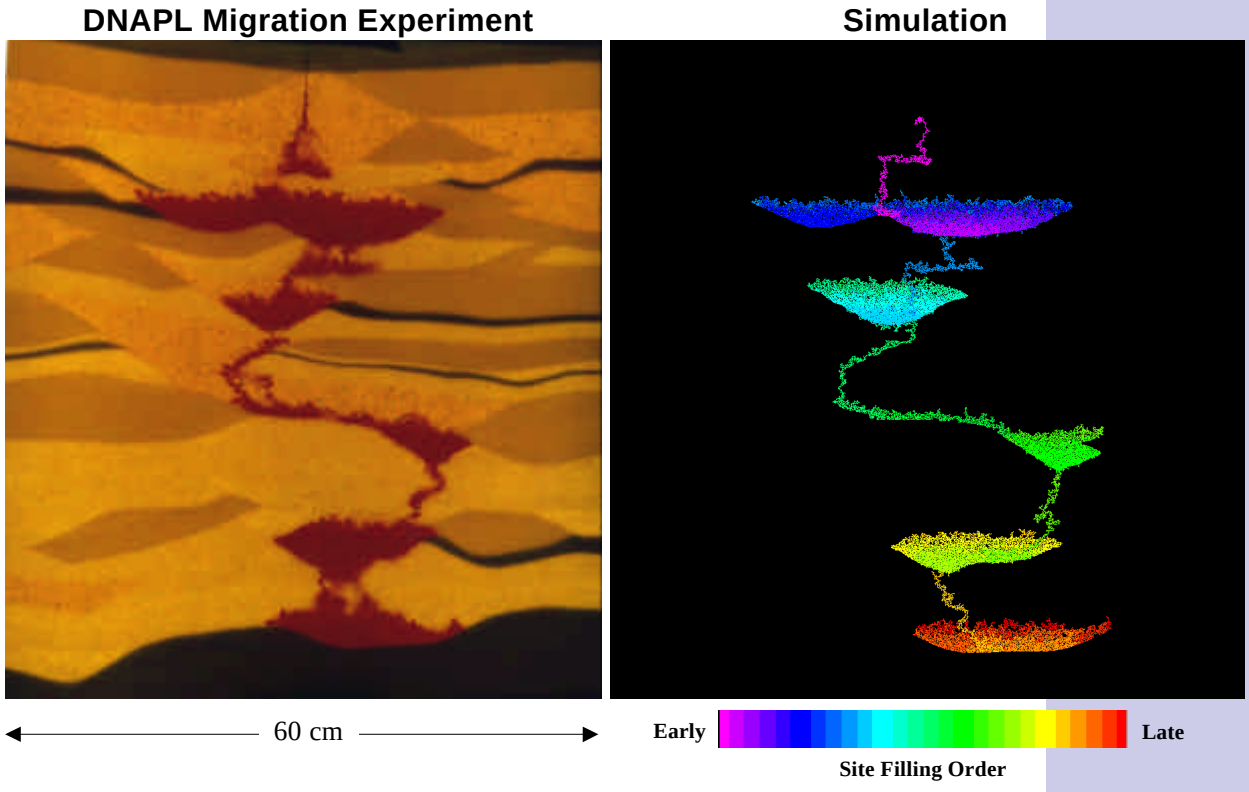
Description: Our work is similar to the work done for EMSP Project #70121, "Influence of Calcium Carbonate Grain Coating on Contaminant Reactivity in Vadose Zone Sediments" with different kinds of cores being examined. We are working to develop a technology/research transfer between the two projects that will be beneficial to both since our respective research

projects are strongly linked and they will jointly provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for tank farm restoration.

Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Dr. John M. Zachara
Collaborating Organization: EMSP project #70121, Influence of Calcium Carbonate Grain Coating on Contaminant Reactivity in Vadose Zone Sediments

Project: 73812 (Renewal of Project 55395)

Title: Physics of DNAPL Migrations and Remediation in the Presence of Heterogeneities
PI: Dr. Stephen H. Conrad *Institution:* Sandia National Laboratories - Albuquerque



Results of a DNAPL migration experiment conducted at Sandia National Laboratories are compared to upscaled percolation modeling. The photo (left) illustrates that the DNAPL(dyed red) migrated downward due to its high density but that aquifer heterogeneities caused significant pooling along the migration path. DNAPL in such a configuration served as the initial condition for remediation experiments. The simulation image (right) compares extremely well with the experiment. [see Project #73812, renewal of #55395]

Description: For the Permanganate experiment, we worked with Dr. Jack Istok, a professor at Oregon State. Flushing with potassium permanganate has been investigated as an oxidizer that mineralizes TCE. Jack suspected that the manganese precipitate that forms as a mineralization product cause permeability reduction and thereby inhibit access between the TCE and the permanganate solution and this is precisely what we were able to visually observe in this experiment. The manganese precipitate formed a low permeability ring surrounding the DNAPL pools. Such results had not been seen previously, because for experiments run in uniform media, the DNAPL does not reside in pools. The permanganate oxidation process not likely to be as efficient as initially hoped in cases where DNAPL resides in pools. Perhaps intermittent flushes with a substance to dissolve away manganese precipitate might be possible.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Jack Istok
Collaborating Organization: Oregon State

Description: The project involves conducting well-controlled laboratory experiments to better understand the physics of DNAPL migration and remediation in the presence of heterogeneities. The results will be used to test and to continue development of new modeling approaches. In addition, the results of the remediation experiments will be used to test the quantitative performance of remediation design codes within heterogeneous media. We intend to work closely with developers of each remediation approach to attempt to optimize the remedial process and show each technique in its best possible light. Towards that end, Alex Meyer, a professor at Michigan Tech, visited our lab and is collaborating with us on our first series of experiments looking at surfactant mobilization and solubilization of DNAPLs.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Alex Meyer
Collaborating Organization: Michigan Tech

Description: For our MA surfactant experiment, we obtained surfactant advice from Alex Meyer and Lirong Zhong. The experiment used the surfactant MA and was designed to maximize solubilization while minimizing mobilization. Contrary to expectation, we observed dramatic mobilization. The DNAPL penetrated the aquitard and became inaccessible to the surfactant. Even though trapping number calculations predict some modest amount of mobilization, failure to account for DNAPL in pools resulted in significantly underestimating the potential for extensive downward mobilization. In observing the mobilization process, we discovered a previously unknown mobilization process that occurs when the surfactant front first encounters a pool. Very different interfacial tensions on either side of the surfactant front result in enhanced drainage of the DNAPL pool. For our particular experimental conditions, due to downward mobilization and penetration of the DNAPL into fine-grained units, introduction of the MA surfactant actually made the problem worse.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Alex Meyer and Lirong Zhiong
Collaborating Organization: Michigan Tech

Description: We worked with Dr. Varadarajan Dwarakanath of Duke Engineering to design the tracer test. It occurred to us that the certain conditions provided by our remediation experiments - subsequent to the emplacement of the DNAPL and prior to beginning the remediation - were ideal for performing a tracer test while requiring very little extra work. Partitioning tracer tests are designed to compare the breakthrough of partitioning and non partitioning tracers. Retardation of the tracers that partition into the organic phase provides a means to calculate the mass of DNAPL contained in the region swept by the tracer test. We found that the test worked qualitatively, indicating the presence of DNAPL, but the calculations significantly underestimated the mass of DNAPL in the chamber. We believe that failure to account for the fact that the vast majority of the DNAPL mass existed in large pools resulted in under-prediction of DNAPL mass. When significant DNAPL mass exists in pools, typical tracer flow rates do not allow sufficient time for partitioning/diffusion of the tracers into and out of large pools.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Varadarajan Dwarakanath
Collaborating Organization: Duke Engineering

Description: The Lead PI has provided consulting services through participation in SCFA, lead lab, and technical assistance teams. On two occasions, he served on teams that dealt with organic contamination of the Ogallala aquifer beneath the Pantex site. He also served on a team that looked at DNAPL contamination at the Stanford Linear Accelerator Center.

Collaboration Type: Consulting *Fiscal Year:* 2001
Collaborating Organization: Subsurface Contaminants Focus Area

Description: For the Tween surfactant experiment, we obtained surfactant advice from Dr. Kurt Pennell, a professor at Georgia Tech. We obtained much better results using the Tween surfactant. We observed only modest DNAPL mobilization because the Tween surfactant maintains a much higher water/organic interfacial tension. We also observed good solubilization. Complete cleanup was achieved after several pore volumes of flushing. Time lapse animation of this experiment yielded important insights into remediation process.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Kurt Pennell
Collaborating Organization: Georgia Tech Microbial Science

Microbial Science

Project: 55264

Title: High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions
PI: Dr. Ernest L. Majer *Institution:* LBNL

Description: The objectives for this project were to develop and apply high-resolution seismic imaging methods for defining physical parameters (lithology, fracture content, fast paths, faults, etc.) that may be controlling flow and transport in naturally heterogeneous material. A primary aspect of the project was to determine if seismic imaging methods could resolve the details necessary to understand the physical heterogeneity controlling microbial behavior. Collaborations are with PNNL and INEEL. PNNL is collaborating in correlating the bacterial behavior to the zones of high permeability detected with the geophysics. INEEL provided the site (TAN) and drilling support as well as collaboration with other EMSP researchers (Colwell and Smith) in understanding the in-situ flow and microbial properties. There were also close collaborations with on site contractors (L. Peterson and T. Woods) in the collection and processing of the data.

Collaboration Type: Consulting *Fiscal Year:* 1999
Collaborator: Dr. Ardeth Simmons, LBL Yucca Mountain PM
Collaborating Organization: Yucca Mountain Project

Description: In our original proposal, we outlined a plan for aggressively addressing issues related to scaling microbiological properties in rock and in pumped groundwater based upon (a) obtaining a large number of transect samples in order to apply geostatistical methods and (b) sampling over volumetric scales that varied by orders of magnitude. Although we worked diligently to obtain these microbiological samples, for a variety of reasons it was not possible to obtain the number or type of either rock or ground water samples from the TAN site. When it became evident our microbiological sample needs could not be met, this project contributed its microbiological resources toward collaboration with another EMSP project (55416) at TAN led by Dr. Rick Colwell. In particular, molecular biological methods were used to characterize microbial communities in core samples from several boreholes (varying in distance from the contaminant injection well) and lithologies, ground water samples from a multilevel sampler in one borehole, and ground water samples obtained during the in situ bioremediation treatment (lactate injection to support anaerobic reductive dehalogenation of TCE).

Collaboration Type: Program interaction *Fiscal Year:* 1999
Collaborator: Dr. Rick Colwell
Collaborating Organization: Idaho National Engineering and Environmental Laboratory

Project: 55416

Title: Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media
PI: Dr. Frederick S. Colwell *Institution:* INEEL

Description: This EMSP research has helped to address EM-40 needs in the cleanup of the waste plume in groundwater by: 1) determining the specific vertical location of contaminants in a model aquifer (the Snake River Plain aquifer) and 2) establishing the presence and distribution of naturally occurring microbial communities that are capable of contaminant degradation. As a

result of this research studies can commence which will focus on estimates of the natural rates of TCE remediation in the aquifer at TAN. This EMSP research has assisted EM-40 and regulatory agencies that have responsibility for the cleanup activities, in determining where aggressive remediation must be conducted and where it is likely that natural attenuation of the contaminants will occur.

Collaboration Type: Consulting
Fiscal Year: 1999
Collaborating Organization: EM-40

Aseptic sampling of fractured rock. [see Project #55416]

Description: The DOE is faced with cleaning up wastes from reactor and weapons production activities during the last fifty years. Many DOE sites have contaminants that are difficult to access due to depth and complex geology and are challenging to degrade using conventional methods. The key objective of this project is to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium with respect to vertical heterogeneities.

Collaboration Type: Consulting
Fiscal Year: 1997
Collaborator: Lance Peterson, Kent Sorenson, and Joe Rothermel
Collaborating Organization: INEEL

Project: 59786

Title: Design and Construction of *Deinococcus radiodurans* for Biodegradation of Organic Toxins at Radioactive DOE Waste Sites
PI: Dr. Michael J. Daly
Institution: Uniformed Services Univ. of the Health Sciences

Description: A cleanup technology is being developed based on the extremely radiation resistant bacterium Deinococcus radiodurans that is being engineered to express bioremediating functions. Research aimed at developing D. radiodurans for organic toxin degradation in highly radioactive waste sites containing radionuclides and heavy metals was started by this group in September 1997. In the United States, only two laboratories have been studying D. radiodurans as their sole research focus over the last ten years; John Battista's lab at LSU, and Daly's group at USUHS. As such, both groups have worked hard at disseminating information and strains, and teaching other labs how to work with this peculiar organism. In the case of

the Daly lab, formal collaborations have been established with the following groups: Jim Fredrickson (PNNL), Larry Wackett (University of MN), Anne Summers (University of GA), Jonathan Trent (NASA Ames Research Center), Owen White (TIGR), Eugene Koonin (NCBI), Jay Keasling (University of CA), and Bob Richmond (Marshall Space Flight Center).

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: (See descriptions)
Collaborating Organization: (See descriptions)

Plant Science

Project: 73843 (Renewal of Project 55118)

Title: Mechanisms of Heavy Metal Sequestration in Soils: Plant-Microbe Interactions and Organic Matter Aging

PI: Dr. Teresa W. M. Fan *Institution:* University of California at Davis

Description: We have initiated collaboration with at Savannah River site (SRS) on uncovering age markers in soil organic matter that are associated with heavy metal sequestration in soils. This information would be valuable towards evaluating metal ion stability in contaminated field sites and directing bioengineering efforts in stabilizing metals and radionuclides at these sites. Using SRS soils, we have successfully prepared 13C- and 15N-labeled organic matter so that the turnover kinetics of various organic matter markers can be followed.

Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. Robin Brigmon
Collaborating Organization: Savannah River Site

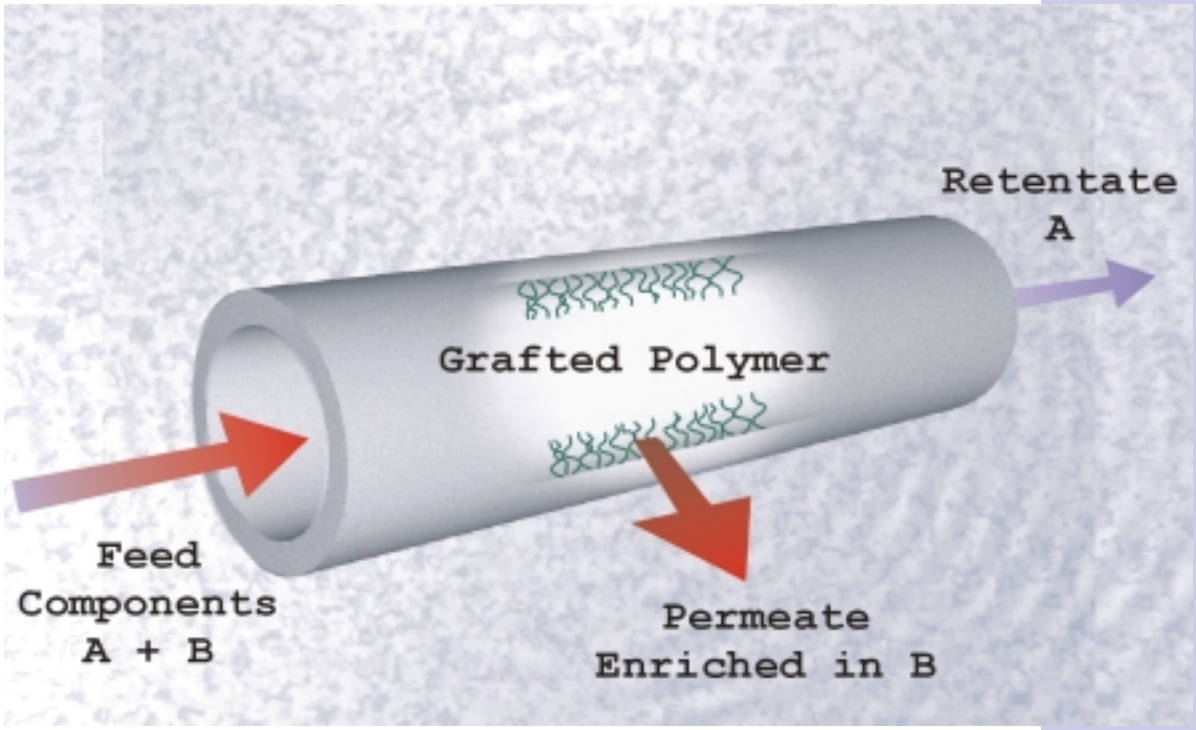
Separations Chemistry

Project: 54926

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

PI: Dr. Yoram Cohen *Institution:* University of California at Los Angeles

Description: There is a growing need in the areas of hazardous waste treatment, remediation, and pollution prevention for new processes capable of selectively separating and removing target organic species from aqueous streams. Membrane separation processes are especially suited for solute removal from dilute solutions. They have the additional advantage of requiring less energy relative to conventional separation technologies (e.g., distillation, extraction, and even adsorption processes). The major difficulty with current membranes is the poor longevity of polymeric membranes under harsh conditions (high temperature, harsh solvents, and pH conditions) and the lack of selectivity of ceramic membranes. In our previous work (1996 EMSP project), a first generation of novel polymer-



Ceramic-Supported Polymer (CSP) Membranes [see Project #54926]

ceramic (PolyCer) composite membranes were developed with the goal of overcoming the above difficulties. The proposed PolyCer membranes are fabricated by a surface-graft polymerization process resulting in a molecular layer of polymer chains which are terminally and covalently anchored to the porous membrane support. We have worked with scientists at the DOE/EMSL facility to characterize the surfaces of our membranes by Atomic Fore Microscopy (AFM) and also by SEM and XPS. We submitted a proposal to EMSL which was accepted. Subsequently, the PI (Dr. Y. Cohen) spent about 4 days at the EMSL facility and his doctoral student (Wayne Yoshida) visited the EMSL facility for a period of three weeks.

Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborating Organization: EMSL

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EMSP Research Transfer

The EMSP provides research resources and results that are intended, in part, to "bridge the gap" between broad fundamental research that has wide-ranging applications such as that performed in the Department's Office of Science, and needs driven applied technology development that is conducted in Environmental Management's Office of Science and Technology. In support of this, the focused research performed in the EMSP is intended to be transferred for utilization by other programs within DOE or to end-users outside the Department.

As research within the EMSP matures, the results from this research should support development of new and innovative ways to reduce risk and cost within EM. In part, the research should address the early, focused research stage of the technology development/deployment cycle for development of new technologies to address cleanup problems within EM. Part of the focus of the EMSP is to integrate the program's research with EM Focus Areas, DOE sites, and commercial interests to support technology development. While much of the research is not yet at a stage of maturity to transfer, many successes have been reported. To date, the reported accomplishments include transfers to:

13 Commercializations
10 Deployments
15 Field Tests
3 Focus Areas and Crosscutting Programs
2 Processes.

Deactivation and Decommissioning

Inorganic Chemistry

Project: 54724

Title: Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach
PI: Dr. Barbara F. Smith
Institution: LANL

Description: Polymer Filtration (PF), which uses water-soluble metal-binding polymers to sequester metal ions in dilute solution with ultrafiltration (UF) to separate the polymers, is a new technology to selectively remove or recover hazardous and valuable metal ions. We have focused on four areas including the development of: (1) synthetic procedures, (2) small ultrafiltration equipment compatible with organic-and aqueous-based combinatorial synthesis, (3) rapid assay techniques, and (4) polymer characterization techniques. We have entered into partnership to use Polymer Filtration in Electroplating industry.

Ultrafiltration unit used in field demonstration for removal of radioactive cations and anions.
[see Project #54724]

Transfer Type: Commercialization - Product *Fiscal Year:* 1999
Contact: NA
Transferring Organization: NA

Materials Science

Project: 60363

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

PI: Dr. James A. Van Den Avyle *Institution:* Sandia National Laboratories

Description: We have conducted a successful technology demonstration with the Russians at a site near Krasnoyarsk (K-26), where they electroslag remelted stainless steel reactor coolant piping that was contaminated with Pu and other radionuclides. The resulting metal ingot was fully analyzed and was clean enough to meet Russian criteria for outside reapplication (sale). We are working with them to obtain significant new funding to set up a full scale commercial melt decontamination facility there to recycle stainless steel. We are also paying for a few additional melts there to further characterize the process.

ElectroSlag Remelting (ESR) process for radioactive decontamination of stainless steel scrap for metal recycle. [see Project #60363]

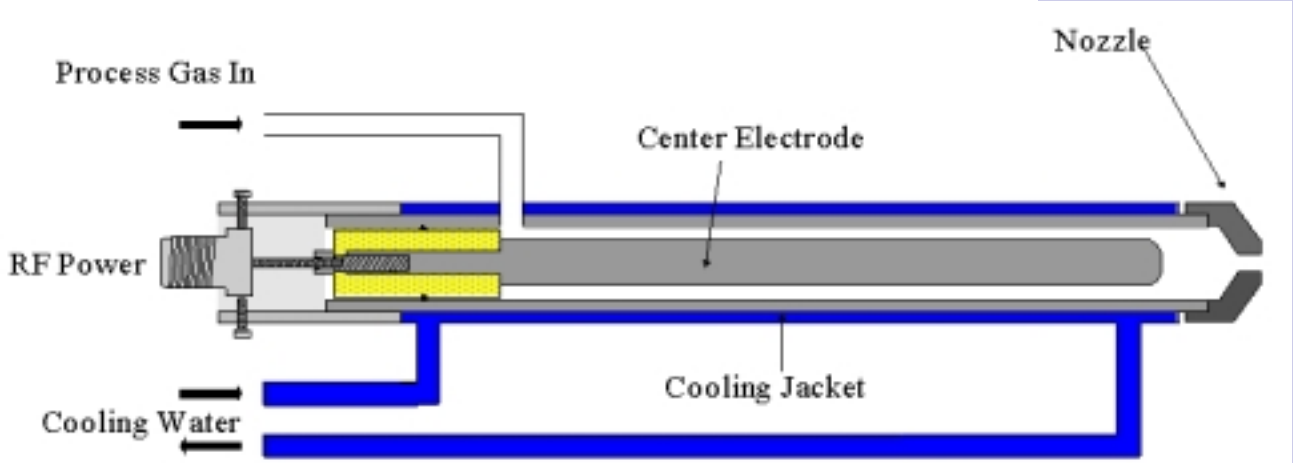
Transfer Type: Process
Fiscal Year: 1999
Contact: James Van den Avyle
Transferring Organization: Sandia National Laboratory

Project: 73835 (Renewal of Project No. 54914)

Title: Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces

PI: Dr. Robert F. Hicks *Institution:* University of California at Los Angeles

Description: After fabricating and testing a prototype plasma decontamination tool, the device will be shipped to the INEEL facility. One post-doctoral scholar will travel to the facility to oversee testing of the plasma device for a specific D&D application. One such application may be the removal of transuranic elements from 1-ft square concrete slabs. In this case, a series of etching experiments will be performed in which the process conditions are varied to obtain the maximum removal rates of TRUs. Air samples will be taken in the vicinity of the process and in the exhaust. These samples will be analyzed to verify that no radioactive waste was released to the surroundings.



Schematic of the first-generation atmospheric-pressure plasma. In this configuration, the process gas is ionized in the annular space between two coaxial electrodes. Then the reactive gas flows out through the nozzle and contacts a work piece placed downstream. [see Project #73835, renewal of #54914]

Transfer Type: Field Test *Fiscal Year:* 2000
Contact: Larry Whitmill
Transferring Organization: INEEL Decontamination and Decommissioning Program

Description: We have made arrangements with TA-55, PF-4 Plutonium Processing Facility and CST-12 Materials Testing Laboratory at LANL for additional testing of our device.
Transfer Type: Field Test *Fiscal Year:* 2000
Transferring Organization: LANL

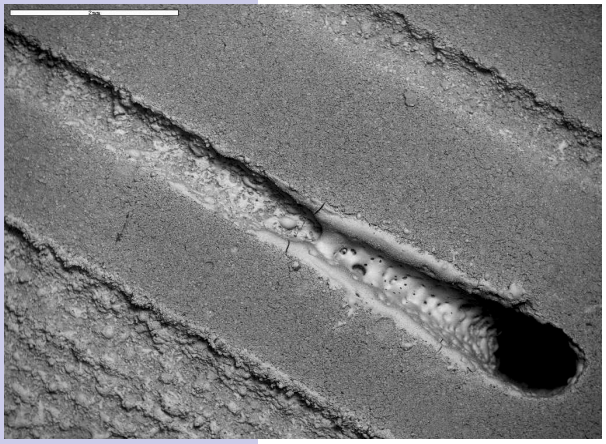
Description: The objective of this project is to identify the key physics and chemistry underlying the use of atmospheric pressure plasmas for etching removal of actinides and actinide surrogates. This includes understanding of basic discharge mechanism at atmospheric pressure, gas and surface phase chemistry, and optimization and scale-up effort of atmospheric pressure plasma jet (APPJ). The plasma source developed under this project has been licensed by Plasma Tech, LLC. The company is currently seeking venture capital financing to develop applications for the semiconductor equipment industry.
Transfer Type: Commercialization - Product *Fiscal Year:* 2000
Transferring Organization: Plasma Tech, LLC

Separations Chemistry

Project: 60283

Title: Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation

PI: Dr. Michael J. Pellin *Institution:* Argonne National Laboratory



Cement surface following Laser Ablation. [see Project #60283]

Description: The objectives of this research are to determine the mechanism and efficacy of laser ablation in removing contaminated surface layers, to understand the chemistry of contaminated concrete surfaces, and to chemically and physically characterize the captured ablation effluent which would become the stored waste. While the focus of this project is on concrete, the technology should be applicable to any surface requiring removal. Efforts are underway to establish a CRADA with Zawtech Inc.

Transfer Type: Commercialization - Product
Fiscal Year: 1999
Transferring Organization: Zawtech Inc.

Project: 64912

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

PI: Dr. David W. DePaoli *Institution:* ORNL

Description: Laboratory-scale experimentation has been aimed at determining improved means for removal of organic contaminants using aqueous surfactant cleaners. We have found that through a simple modification of process conditions, the rate of oil removal can be significantly increased. We have communicated, through a non-disclosure agreement, an invention based on our findings with a leading company that produces industrial cleaners. That company has agreed to collaboratively participate in testing of the technology through guidance and evaluation.

Transfer Type: Commercialization - Product *Fiscal Year:* 2000
Contact: David DePaoli
Transferring Organization: Undisclosed at this time

HEALTH/ECOLOGY/RISK

Health/Risk

Project: 74050 (Renewal of Project No. 59882)

Title: Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at US DOE Fernald

PI: Dr. Naomi H. Harley *Institution:* New York University Medical School

Description: The research is directed to developing state-of-the-art personal and environmental exposure assessment for inhaled radionuclides. The research is conducted at Fernald and the specific nuclides of interest are radon (Rn-222), and thoron (Rn-220) emission from the silos, and thorium-230, 232 airborne aerosol particles from the waste pits. Two new instruments are being used at Fernald, and have been deployed for about 1 year. Together they permit the air concentrations of the gas, the airborne particulates, and their particle size distribution to be measured on a continuous basis. The new instruments developed can have wide application at other DOE sites.

The first insturment is a radon, thoron passive alpha track detector that can be worn or used as an area detector to obtain research quality measurements for modeling or personal exposure assessment. Thoron measurements are not commonly made and little data are available. Measurements at Fernald with simultaneous measurements at research homes in the New York, New Jersey area show that essentially all radon measurements contain a fraction of thoron. NYU is currently seeking a patent for this detector. Plans are to modify the existing model to have 4 detection chambers rather than 3, so that duplicate measurements of both radon and thoron can be made simultaneously.

The second insturment is a particle size analyzer. Although the inhaled particle size is the major determinant of bronchial dose, Fernald is the only site attempting to do particle size distribution measurements. Prior to the development of this instrument, the labor intensive effort needed, as well as the cost, precluded the measurement. The particle size analyzer presently supplies airborne particulate concentration and size data at the waste pits, the soil dryer, and at buildings being removed. A wider network of analyzers is being deployed to study resuspension and transport of particles.

Radon thoron detector, as it would be used in the field of personal monitoring. [see Project #74050, renewal of #59882]

Transfer Type: Deployment - Product
Fiscal Year: 2000
Transferring Organization: Department of Energy - Fernald

HIGH-LEVEL WASTE

Actinide (Heavy Element) Chemistry

Project: 73749 (Renewal of Project No. 54621)

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

PI: Dr. Andrew R. Felmy *Institution:* Pacific Northwest National Laboratory

Description: EMSP research has yielded thermodynamic data that is the instrumental developing the Pitzer Model in Environmental Simulation Program (ESP). This new thermodynamic model predicts the dissolution and precipitation of solids important in tank processing and cross-site transfer line plugging. The Pitzer model is more robust in terms of the thermodynamic approach used and also allows the model database to be upgraded in a much more efficient and systematic fashion. The database upgrade is possible since virtually all scientific publications throughout the world now interpret and publish their aqueous thermodynamic results using the Pitzer theory. Access to such a wealth of available data generated under numerous DOE and other programs including the EMSP, the Waste Isolation Pilot Plant (WIPP), and the Office of Science (OS) will significantly improve tank process modeling at Hanford. ESP used by all of the contractors at the Hanford and Savannah River sites.

Transfer Type: Deployment - Product *Fiscal Year:* 2001

Transferring Organization: Savannah River and Hanford Sites

Analytical Chemistry & Instrumentation

Project: 60424

Title: High Temperature Condensed Phase Mass Spectrometric Analysis

PI: Dr. James E. Delmore *Institution:* INEEL

Description: The goal of this project was to develop an integrated mass spectrometric analysis system capable of analyzing materials from room up to high temperatures, with the practical upper temperature limit to be experimentally determined. A primary objective of the program was the development of techniques to analyze waste materials during vitrification processing to produce waste forms. As a result of this research, this analytical tool is now being used here at INEEL to support subsurface science research. The tool is capable of performing mass spectral analysis on solid surfaces. It performs multiple analyses in rapid succession versus the current tools which utilize single analytical techniques.

Transfer Type: Deployment *Fiscal Year:* 2001

Transferring Organization: Idaho National Engineering and Environmental Laboratory

Engineering Science

Project: 60143

Title: Foaming in Radioactive Waste Treatment and Immobilization Processes
PI: Dr. Darsh T. Wasan *Institution:* Illinois Institute of Technology

Description: The new antifoam has proved to be superior to the current antifoam agent. A series of recent tests was completed to determine whether radioactivity would make the antifoam ineffective by fragmenting it. However, it seems to be resistant to the radiation fields expected in radioactive operations. A vendor has been identified who will produce the antifoam agent for Defense Waste Processing Facility (DWPF). DWPF expects to implement the new antifoam agent before the end of CY00. There is a need for new or improved antifoam agents in a variety of SRS processes including Waste Tank evaporation, Sludge processing, and Salt processing. Other DOE sites with similar evaporation processes, primarily Hanford, ORNL, and INEEL are all in need of better antifoam agents. We need to work closely with them to accomplish these goals.
Transfer Type: Deployment - Product *Fiscal Year:* 2000
Transferring Organization: Department of Defense - Defense Waste Processing Facility

Description: The improved antifoam agent developed by the IIT researchers based on a better understanding of the chemistry, rheology, and physics that lead to the formation of foam during waste processing was successfully tested in laboratory scale experiments at both IIT and SRS and in a pilot plant at SRS. The methodology for developing a new antifoam agent for Defense Waste Processing Facility (DWPF) can now be used to develop other antifoam agents to support other DOE sites, especially Hanford.
Transfer Type: Field Test *Fiscal Year:* 2000
Contact: Dan Lambert
Transferring Organization: Savannah River Site

Project: 65371

Title: Numerical Modeling of Mixing of Chemically Reacting, Non-Newtonian Slurry for Tank Waste Retrieval
PI: Dr. David A. Yuen *Institution:* University of Minnesota

Description: Under this project, PNNL has successfully integrated a computational fluid dynamics code with state-of-the-art equilibrium and kinetic chemical models and non-Newtonian rheology. This new transport code, ARIEL, is a state-of-the-art non-Newtonian reactive transport computer code that is applicable to a time-varying, three-dimensional hydrothermal field with multi-phase, multi-component, high ionic-strength, and highly basic chemical conditions. This is unique and is already being applied to the complex phenomena of tank waste retrieval. The ARIEL code explicitly accounts for interactions of aqueous chemical reactions, adsorption/desorption, and dissolution/precipitation under high ionic-strength conditions and associated rheology (viscosity and yield strength) changes.

Developments in this project including computer code and staff expertise are being applied directly to TFA needs. The ARIEL code was used to model the mixing of waste with two 300-hp mixer pumps in Hanford's Double-Shell Tank 241-AZ-102 and is currently being applied to 241-AN-104 and 241-AN-105 for Hanford's W211 (Tank Waste Retrieval) Project.

Transfer Type: Deployment - Product *Fiscal Year:* 2001
Transferring Organization: Hanford W211 (Tank Waste Retrieval) Project

Project: 81897 (Renewal of Project No. 65435)

Title: Millimeter-Wave Measurements of High Level and Low Activity Glass Melts
PI: Dr. Paul P. Woskov *Institution:* Massachussettes Institute of Technology

Description: This project is organized as a collaborative effort that can serve as a model for the EMSP program. It includes a University (MIT) with experience in innovative diagnostic technologies, a national laboratory (PNNL) with expertise in glass and materials science, and a national end user laboratory (SRTC) which develops and operates waste glass vitrification facilities. Furthermore, we participate with the Tank Focus Area in pilot scale testing, i.e. the recent melter tests at Clemson Environmental Technology Laboratory (CETL). Future field tests of the Milliwave Viscometer are being planned.

The cross fertilization of expertise of the research partners on this project is resulting in award winning innovation that is highly focused to the EMSP mission. In addition, there may be significant commercial spin off applications to the glass manufacturing and metals refining industries.

Transfer Type: Field Test *Fiscal Year:* 2001
Transferring Organization: Tanks Focus Area

Separations Chemistry

Project: 73803 (Renewal of Project No. 55087)

Title: Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation
PI: Dr. Bruce A. Moyer *Institution:* ORNL

Description: The role of the EMSP project in my lab entailed performing a fundamental investigation of the mechanism of cesium extraction so as to understand the nature of the complexes formed between the cesium ion and the extractant molecule. This fundamental information played a crucial role in the successful process development under ESP funding. Indeed, without the fundamental information providing the needed insight at just the right time, the process development would have failed to advance fast enough to meet the emergency need to test new technology at the SRS.

Transfer Type: Focus Area - Process *Fiscal Year:* 1999
Contact: Bruce Moyer
Transferring Organization: ORNL

Description: Owing to the high levels of radiation and heat generated by the fission-product Cs-137, efficient cesium separation from high-level wastes (HLWs) has been elevated to extreme importance at Hanford, the SRS (SRS), and Idaho Falls, where multi-billion dollar projects will carry out this and other HLW separations. Referred to as Alkaline-Side CSEX (Cesium Solvent Extraction), the ORNL invention (U.S. Pat. Appl. 60/057,974, September 3, 1998) provides the first practical application of calixarene-crown extractants to treatment of HLWs by solvent extraction. An effective form of the extractant was first synthesized at ORNL and recently transferred to the commercial sector. Batch tests on actual HLW by collaborators at both Hanford and the SRS in the past year have confirmed the effectiveness of the ORNL process, and a 24-stage centrifugal-contactor demonstration at Argonne National Laboratory proved economic viability. Results from the batch and engineering tests showed that stringent requirements of a 40,000-fold reduction in Cs-137 activity in the waste and a 12-fold concentration can be readily met. In addition to meeting these SRS decontamination and concentration needs, key advantages of the ORNL process include the following: (1) The process does not require adjustment of the waste feed stream. (2) Extraction is very selective. (3) Scrubbing and stripping of the solvent can be accomplished with very dilute acidic solutions. (4) The process is compact and involves liquid streams. These advantages reduce costs by minimizing consumption of chemicals, secondary waste production, volume of vitrified waste form, and plant space. The cesium-concentrated stream produced by the process is expected to be so pure that it will require negligible downstream processing and will have negligible impact on the volume of the final vitrified waste form, which is costly to produce and store.

Transfer Type: Commercialization - Process *Fiscal Year:* 1999
Transferring Organization: IBC Advanced Technologies

Description: Westinghouse Savannah River Corporation is conducting tests of alternative technologies for the removal of cesium from its high-level waste and has evaluated the alkaline-side CSEX process as an alternative technology for replacement of the in-tank precipitation process. Successful evaluation will result in further development, scale-up, demonstration, and pilot-scale testing. Ultimately, the goal is implementation in a billion-dollar plant.

We are supplying this customer with information on the alkaline-side CSEX process and responding to customer requests for tests and report results (Note that the PI's ESP task was leading this activity. EMSP's role was in supplying basic scientific information that was useful in development of the process and in understanding process behavior.).

In Nov. and Dec. 1999, the customer at the SRS has shown intense interest in further development of the alkaline-side CSEX process by requesting input for creation of a work-scope for engineering evaluation at the $2-4M level in FY 2000 and FY 2001. In Feb. 2000, DOE approved a $3M task funded through WSRC and led by ORNL for accelerating the development and testing of the alkaline-side CSEX process for possible

application in the removal of cesium from high-level salt waste. ORNL, WSRC, and ANL have assembled teams, organizational structure, and plans to carry out this task. This project has been in progress and will continue through June, 2001. Interaction among the ORNL, WSRC, and ANL teams has been daily, with several conference calls each week, numerous reports, numerous presentations, and daily individual interactions. As of September 2000, test results are very positive, and the CSEX process appears competitive with the other two alternative technologies.

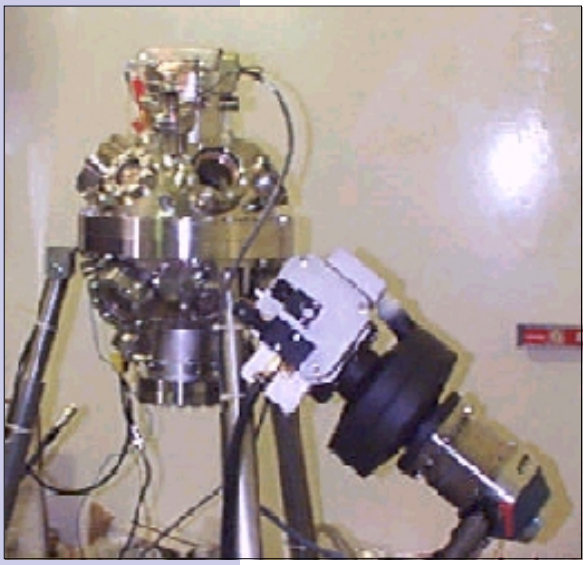
Transfer Type: Focus Area - Process *Fiscal Year:* 2000
Transferring Organization: Westinghouse Savannah River Corporation

MIXED WASTE

Analytical Chemistry & Instrumentation

Project: 54751

Title: High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste
PI: Dr. Mark M. Pickrell *Institution:* LANL



Two commercial partners have applied for a license for the High Fluence Neutron Source, shown here in the laboratory. [see Project #54751]

Description: We are addressing the need to measure nuclear wastes, residues, and spent fuel in order to process these for final disposition. One of the primary methods for waste assay is by active neutron interrogation. We plan to improve the capability of all active neutron systems by providing a higher intensity neutron source (by about a factor of 1,000) for essentially the same cost, power, and space requirements as existing systems. We have received 2 request from commercial vendors to commercialize this technology once available.

Transfer Type: Commercialization - Product
Fiscal Year: 1999
Contact: Manfred Frey, Michael Hurwitz
Transferring Organization: MF Physics, Inc., Gamma Metrics, Inc.

Project: 73844 (Renewal of Project No. 60231)

Title: Miniature Chemical Sensor Combining Molecular Recognition with Evanescent-Wave Cavity Ring-Down Spectroscopy
PI: Dr. Andrew C. R. Pipino *Institution:* National Institute of Standards & Technology - Maryland

Description: A entirely new class of chemical sensors is being developed that will enable qualitative and quantitative remote, real-time, optical diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases through a

completely novel implementation of cavity ring-down spectroscopy. Negotiations with a commercial partner are in progress.
Transfer Type: Commercialization - Product *Fiscal Year:* 1999
Transferring Organization: Not disclosed at this time

Description: A Cooperative Research and Development Agreement (CRADA) is being negotiated to develop and build prototype, portable, miniature spectrometers, which will be fiber-optic-coupled to inexpensive diode laser sources.
Transfer Type: Commercialization - Product *Fiscal Year:* 1999
Transferring Organization: Informed Diagnostics, Inc

Description: Discussing deployment of miniature spectrometer at the SRS for groundwater monitoring.
Transfer Type: Focus Area -Product *Fiscal Year:* 1999
Contact: Michael G. Serrato
Transferring Organization: SRS

Separations Chemistry

Project: 54571

Title: Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods
PI: Dr. Nelly M. Rodriguez *Institution:* Northeastern University

Description: Graphite nanofibers are a newly developed type of material that can be synthesized by the decomposition of selected hydrocarbons over selected metal particle surfaces. The structural characteristics of the solid can be manipulated by a careful selection of parameters including the catalyst, the reaction conditions and the temperature. Both the size and the morphology of the metal particle have been found to play an important role on the cross-sectional area as well as the orientation of the graphene sheets. It is therefore possible to produce materials where the platelets are aligned either parallel, perpendicular, or at an angle with respect to the fiber axis. The consequence of the interplay between particle and morphology is that a variety of conformations are possible including tubular, ribbon-like, or structures where only edges of the basal plane are exposed. Graphite nanofibers are usually produced in bulk quantities using unsupported metal powders, having an average particle size of ~1 nm. The cross-sectional area of the resulting fibers exhibit a large range usually between 5 to 100 mm, as a result of uneven fragmentation of the original particles during the reaction. In our current program, we have attempted to generate nanofibers of controlled dimensions in order to produce material having both a high surface area and a high electrical conductivity that results from a long range crystallographic order.


Researcher characterizing sample by TEM. [see Project #54571]

Discussions have been conducted with both Corning Inc. and W. R. Grace, who have expressed an interest in the commercial prospects of the technology being developed in the program at Northeastern University. The synthesis of carbon nanostructures has been optimized at the laboratory scale and it is anticipated that the large scale production of the material will be undertaken by various companies.

Transfer Type: Commercialization - Process *Fiscal Year:* 2000
Transferring Organization: Corning, Inc. and W. R. Grace

Description: Due to the potential for applications in a variety of energy related areas, Catalytic Materials Ltd., a small company based in Pennsylvania has decided to undertake the further development of these materials.

Transfer Type: Commercialization - Product *Fiscal Year:* 2000
Transferring Organization: Catalytic Materials, Ltd.

NUCLEAR MATERIALS

Engineering Science

Project: 60077

Title: Development of Nuclear Analysis Capabilities for DOE Waste Management Activities
PI: Dr. Cecil V. Parks *Institution:* OR NL

Description: It is desired to fully implement the computational techniques developed in this project for global distribution through the Standardized Computer Analyses for Licensing Evaluation (SCALE) code system. SCALE is widely used throughout the nuclear safety community. Several nuclear criticality safety organizations have expressed interest in using the SEN3 analysis tool in conjunction with the S/U methodology developed under NRC and DOE Nuclear Criticality Safety Program projects. Both the NRC and DOE OCRWM/YMP are very interested in the application of the SAS2D depletion sequence developed based on NEWT for spent nuclear fuel analysis.

Several nuclear safety organizations have expressed interest in using these new analysis tools and techniques for their applications. Some work has already been performed by ORNL for INEEL for the storage and transport of DOE-owned highly-enriched uranium fuels, and INEEL has expressed interested in obtaining this software for in-house use involving classified systems when a release version is available. Interest in the use of these methods has been specifically expressed by those associated with the Yucca Mountain Project and the Savannah River Site.

Transfer Type: Deployment - Product *Fiscal Year:* 2001
Transferring Organization: Department of Energy - ORNL

SUBSURFACE CONTAMINATION

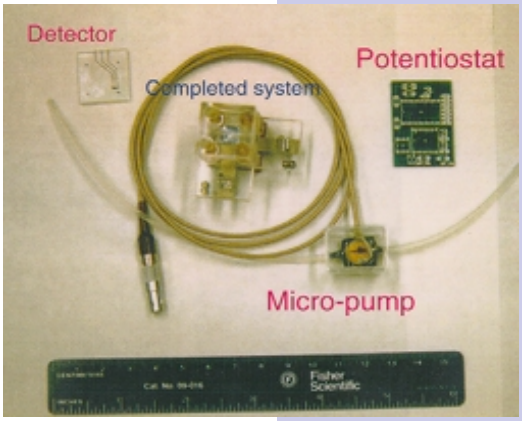
Analytical Chemistry & Instrumentation

Project: 54639

Title: Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites

PI: Dr. Joseph Wang *Institution:* New Mexico State University

Description: This project has led to the replacement of conventional, lab-based, electrochemical stripping protocols and systems with new innovative strategies for field monitoring of trace chromium and uranium, based on micromachined hand-held total stripping analyzers, in-situ sensing devices, and submersible microsystems. These efforts have resulted also in two joint (NMSU-PNL) patents covering the remote-sensor and probe technologies which have been licensed Instrumentation Northwest Inc. (of Richland). New Mexico State University and PNL are working closely on transferring these in-situ metal technologies and realizing their rapid commercialization.



NMSU / PNNL Electrochemical Metal Microanalyzer [see Project #54639]

Transfer Type: Commercialization - Product
Fiscal Year: 2000
Transferring Organization: Instrumentation Northwest Inc., Richland, WA

Biogeochemistry

Project: 55388

Title: Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents

PI: Dr. Neil C. Sturchio *Institution:* ANL

Description: The purpose of this project was to investigate the potential applications of stable isotope ratio measurements in characterization of the source terms, the transport, and the fate of chlorinated solvents in groundwater aquifers. The approach to this research was threefold: (1) to develop methods for the sampling and isotopic analysis of chlorinated solvents in groundwaters; (2) to perform laboratory experiments to measure equilibrium and kinetic isotope effects associated with biological and physical transformation processes of chlorinated solvents; and (3) to perform field investigations at well-characterized, contaminated aquifer sites to demonstrate the applicability of the isotopic approach in real-world situations. A method for stable isotope analysis of carbon and chlorine in chlorinated aliphatic hydrocarbons developed through this project has been adapted by several laboratories (e. g., University of Nevada, Reno, NV; University of Waterloo, Canada; University of Reading, U.K.; Environment Centre of the Joint European Commission, Ispria, Italy).

Transfer Type: Process *Fiscal Year:* 2000
Contact: (see description)
Transferring Organization: (see description)

Description: Methods developed during this project were applied in conjunction with remedial activities for TCE-contaminated groundwater aquifers carried out by Lockheed-Martin Energy Systems, Inc. at the Paducah Gaseous Diffusion Plant in Kevil, KY.
Transfer Type: Field Test *Fiscal Year:* 2000
Contact: Jay Clausen
Transferring Organization: Lockheed-Martin Energy Systems, Inc.

Description: Methods developed during this project were applied in conjunction with remedial activities for TCE-contaminated groundwater aquifers carried out by ENSR, Inc. (Westmont, IL) at locations in the Chicago, IL; Kansas City, MO; and Greer, SC areas.
Transfer Type: Field Test *Fiscal Year:* 2000
Contact: Greg Smith
Transferring Organization: ENSR, Inc. (Westmont, IL)

Engineering Science

Project: 70088

Title: Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone
PI: Dr. Baolin Deng *Institution:* New Mexico Institute of Mining & Technology

Description: Laboratory investigations conducted over the last several years indicate that reduction and immobilization of chromium in contaminated soil can be achieved in situ through treatment with a diluted hydrogen sulfide gas mixture. The primary chemical reaction of interest associated with these tests involves the reduction of Cr(VI)to Cr(III),with subsequent precipitation as a nontoxic solid product. Immobilization of radionuclides, such as technetium and uranium, and heavy metals, such as mercury and lead are other potential applications of the In Situ Gaseous Reduction (ISGR)approach to vadose zone remediation.

The application of diluted hydrogen sulfide to chromium reduction in the field can be accomplished through the injection of the gas mixture into waste site soils in a central borehole. The gas mixture is then drawn through the waste site by vacuum applied at extraction boreholes located at the site boundary. A successful small scale demonstration of the ISGR approach has been completed at White Sands Missile Range in a joint DOE-DoD field test. This test showed:

- 70%of Cr(VI)in the vadose zone immobilized
- H S gas mixture can be safely handled
- Excess H 2 S is largely consumed by interaction with soil,no releases to the environment

Transfer Type: Field Test *Fiscal Year:* 2001
Transferring Organization: Department of Energy and Department of Defense

Project: 73793 (Renewal of Project No. 55013)

Title: Biofiltration of Volatile Pollutants: Solubility Effects
PI: Dr. Brian H. Davison *Institution:* Oak Ridge National Laboratory

Description: We have had several requests from researchers and practitioners for access to our Biofilter software, primarily so they can apply it to the particular systems with which they work. Examples include Gero Leson of Berkeley, California, who is an independent contractor specializing in industrial biofilter applications and William Apel of the Idaho National Environmental and Engineering Laboratory, who conducts directed research in degradation of industrial VOCs.
Transfer Type: Deployment - Product *Fiscal Year:* 2000
Contact: (See description)
Transferring Organization: (See description)

Geophysics

Project: 55332

Title: A Hybrid Hydrologic-Geophysical Inverse Technique for the Assessment and Monitoring of Leachates in the Vadose Zone
PI: James R. Brainard *Institution:* Sandia National Laboratories - Albuquerque

Description: The objective of this study is to develop and field test a new, integrated Hybrid Hydrologic-Geophysical Inverse Technique (HHGIT) for characterization of the vadose zone at contaminated sites. This new approach to site characterization and monitoring can provide detailed maps of hydrogeologic heterogeneity and the extent of contamination by combining information from 3D electric resistivity tomography (ERT) and/or 2D cross-borehole ground penetrating radar (XBGPR) surveys, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data. The project is involved conducting a field test of the HHGIT at the Sandia/Tech Vadose Zone Facility in Socorro, New Mexico. We are currently processing the data and will be publishing results later this year. Investigators in the project also participated in the Advanced Characterization Workshop at Hanford in January of 2000, and have been in contact with the Tank Focus Area about performing a similar test at the Hanford Reservation.
Transfer Type: Field Test *Fiscal Year:* 2000
Transferring Organization: Sandia National Laboratory

Project: 60162

Title: Enhancements to & Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument & Applications to Shallow Subsurface Imaging at Sites in the DOE Complex
PI: Dr. David L. Wright *Institution:* U.S. Geological Survey - Denver

Description: The U.S. Geological Survey and the University of Illinois propose to improve the state-of-the-art electromagnetic imaging of the shallow (0 to 5 m) subsurface in conductive media with potential applications to subsurface characterization, landfill stabilization, decontamination/decommissioning, and waste characterization at sites in the DOE complex. We plan to accomplish the research objectives by a combination of hardware and software enhancements to the existing Very Early Time Electromagnetic (VETEM) prototype instrument, physical modeling experiments, numerical forward and inverse modeling, and field demonstrations. We will enhance the existing system with additional antennas, transmitter options, and most likely one or more gradiometer configurations, as well as a modified receiver. The VETEM prototype system has been to INEEL twice since the beginning of our EMSP funding. The first trip, in July 1998, entailed a demonstration at the Cold Test Pit. The second trip was in Nov-Dec of 1998 to do a survey of Pit 9.

Transfer Type: Field Test *Fiscal Year:* 1999
Contact: Aran Armstrong & George Schneider
Transferring Organization: INEEL

Project: 73836 (Renewal of Project No. 55300)

Title: Induced Polarization with Electromagnetic Coupling: 3D Spectral Imaging Theory and Field Tests
PI: Dr. F. Dale Morgan *Institution:* Massachusettes Institute of Technology

Description: The Earth Resources Laboratory (ERL) has made recent advances in applying the Induced Polarization (IP) method for detection and mapping of contaminant plumes. The project encompassed laboratory studies of microgeometry and chemistry effects on Induced Polarization (IP), an investigation of electromagnetic coupling (emc) noise, and development of 3D modeling and inversion codes. In a competitive review of number of EMSP characteriztion projects this projects was selected to demonstrate plume mapping capabilites. The field effort proved to be very difficult, but seems to have yielded good results. The processed data has matched well with some lab results and picture. Continutation work is planned for this effort.

Transfer Type: Field Test *Fiscal Year:* 2001
Contact: Brian Looney
Transferring Organization: Savannah River Site

Project: 73962 (Renewal of Project No. 60115)

Title: Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface
PI: Dr. Alan Levander *Institution:* Rice University

Description: The objective of this project is to develop and test advanced near vertical to wide-angle seismic methods for structural imaging and material properties estimation of the shallow subsurface for environmental characterization efforts. We have conducted a high resolution seismic profile for

subsurface characterization at a DNAPL site at a DOD facility in August 1998. Currently, the data is being processed and we are planning to return to the site for additional work.

Transfer Type: Field Test *Fiscal Year:* 1999
Transferring Organization:

Hydrogeology

Project: 55036

Title: Colloid Transport and Retention in Fractured Deposits
PI: Dr. John F. McCarthy *Institution:* ORNL

Description: The rates and extent of colloid and water movement was determined in fractured porous media at Waste Area Group 5 of the ORNL and at a site in Bear Creek Valley near waste disposal areas of the Oak Ridge Y-12 Plant. The data are directly relevant to assessments of risk from the migration of transuranic radionuclides, and in evaluation of remedial options.

Transfer Type: Field Test *Fiscal Year:* 2000
Contact: Dr. John McCarthy
Transferring Organization: ORNL

Project: 55196

Title: In Situ, Field Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well, Push-Pull Test
PI: Dr. Jonathan D. Istok *Institution:* Oregon State University

Description: An innovative new site-characterization technology termed the single-well, "push-pull" test method was used for this study. This technology has been the recent subject of development at Oregon State University because it can be used in the field to determine a wide range of aquifer physical, chemical, and biological characteristics. A push-pull test consists of the controlled injection of a prepared test solution into a single monitoring well followed by the extraction of the test solution/groundwater mixture from the same well. This technology was field tested at the Idaho National Engineering and Environmental Laboratory in the FY01 and the data gathered is being analyzed. An other field test is scheduled in the spring of 2002.

Transfer Type: Field Test *Fiscal Year:* 2001
Transferring Organization: INEEL

Project: 60158

Title: Development of Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface
PI: Dr. Lewis Semprini *Institution:* Oregon State University

Description: The objective of this research is to develop a unique method for using naturally occurring radon-222 as an inexpensive partitioning tracer for locating and quantitatifying nonaqueous phase liquid (NAPL) contamination in the subsurface, and assessing the effectiveness of NAPL

remediation. Laboratory, field, and modeling studies are being performed to evaluate this technique and to develop methods for its successful implementation in practice. We have conducted Radon-222 and Surveys at Site-300 at the LLNL. This site is highly contaminated with TCE. The radon results were encouraging, and indicated a zone of NAPL likely existed.

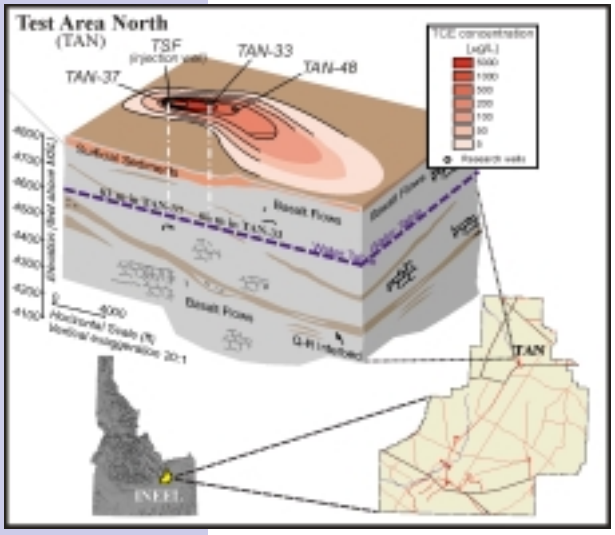
Transfer Type: Field Test *Fiscal Year:* 1999
Contact: Rolf Halden (925-422-0655 or halden1@llnl.gov)
Transferring Organization: LLNL

Microbial Science

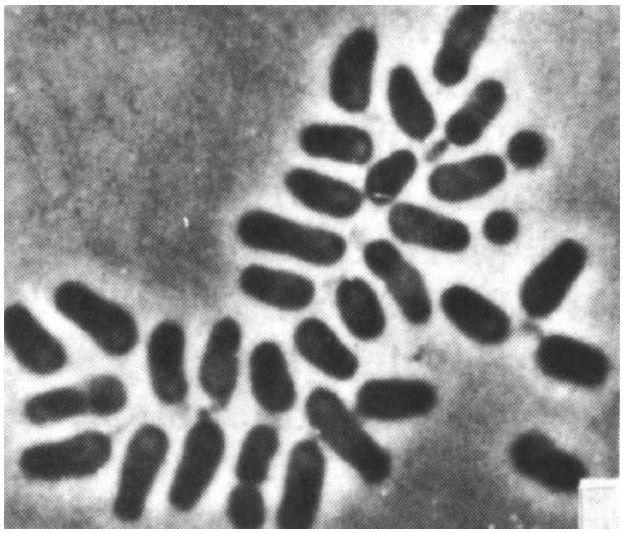
Project: 55264

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

PI: Dr. Ernest L. Majer *Institution:* LBNL



Microorganisms with the capability of degrading dissolved TCE in the fractured basalts beneath the INEEL Test Area North are being studied to determine their vertical distribution and to assess how geohydrological factors associated with this complex subsurface environment control their activities. [see Project #55416]



Naturally-occurring TCE-degrading microorganisms may naturally attenuate the TAN TCE plume at low concentrations. [see Project #55416]

Description: We have been using our technology at the TAN site at INEEL to aid in defining the plume movement and location.

Transfer Type: Field Test *Fiscal Year:* 1999
Contact: Tom Woods and John Bukowski
Transferring Organization: Parsons

Project: 55416

Title: Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media
PI: Dr. Frederick S. Colwell
Institution: INEEL

Description: The key objective of this research is to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium with respect to vertical heterogeneities. To determine whether microbial degradation is spatially correlated to preferred flow paths for the contaminant and required electron donors and acceptors we will characterize the biological and abiological properties of cores and samples from multi-level samplers placed in the same borehole. We will use a combination of traditional microbiological methods (e.g., enrichments) and molecular tools to characterize the indigenous microbial communities. During a project that involved coring and well completion of TAN-48 (INEEL) the effect of lactate-induced bioremediation were characterized.
Transfer Type: Field Test
Fiscal Year: 1999
Contact: Lance Peterson, Kent Sorenson, and Joe Rothermel
Transferring Organization: LMITCO and Parsons

Plant Science

Project: 70054 (Renewal of Project No. 54837)

Title: Phytoremediation of Ionic and Methyl Mercury Pollution
PI: Dr. Richard B. Meagher
Institution: University of Georgia

Description: Our long-term goal is to enable highly productive plant species to extract, resist, detoxify, and/or sequester toxic heavy metal pollutants as an environmentally friendly alternative to physical remediation methods. We have focused this phytoremediation research on soil and water-borne ionic and methylmercury. We engineered several plant species (e.g., Arabidopsis, tobacco, canola, yellow poplar, rice) to express the bacterial genes, merB and/or merA, under the control of plant regulatory sequences. These transgenic plants acquired

Mercury-eating plants developed by this project absorb mercury through their roots, then release it in a less toxic form through their leaves. [see Project #70054, renewal of #54837]

Hygromycin selection of merA and merB transformed rice shoots and plants from embryogenic calli. A growth comparison of a wild-type to a hyg resistant (HygR) transformed plantlet left two weeks on 30 mg/l hygromycin. [see Project #70054, renewal of #54837]

remarkable properties for mercury remediation. Our project has been so successful that a private company, PhytoWork Inc., has been created.

Transfer Type: Commercialization - Business
Fiscal Year: 1999
Contact: Richard Meagher
Transferring Organization: PhytoWork Inc.

Separations Chemistry

Project: 54926

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

PI: Dr. Yoram Cohen *Institution:* University of California at Los Angeles

Description: Growing interest by industry in the PolyCer membrane concept is encouraging. With additional optimization work, we are confident that PolyCer membranes will emerge to meet the demand for membranes that retain their structural integrity and longevity under harsh conditions while maintaining the desired selectivity and permeate flux. The approach will pave the way for a rapid tailor-design of pervaporation and UF membranes for organic-aqueous separations. We are currently negotiating with a company called Spinktek Filtration regarding the use of our technology for making non-fouling membranes.

Two other companies (Pervatech in the Netherlands and Asahi Chemical Industry in Japan) signed secrecy agreements with UCLA in connection with our project.

Transfer Type: Commercialization - Product *Fiscal Year:* 2000
Transferring Organization: Spinktek Filtration

EMSP Student Research

One goal of the EMSP is to serve as a stimulus to focus the nation's science infrastructure on critical national environmental management problems. One of the primary ways to accomplish this goal is to increase the cadre of scientific expertise available to focus on EM problems. By making opportunities available for Post Doctoral, Ph.D., Masters, and Undergraduate research on EMSP projects, the program achieves this goal. EMSP currently supports the following number of student researchers:

103 Undergraduate Researchers
260 Master Researchers
69 Ph.D. Researchers
184 Post Doctoral Researchers.

The tables below describe the EMSP's accomplishments in the area of undergraduate, graduate, and post-graduate research support as reported in project annual and final reports.

Deactivation and Decommissioning

Biogeochemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
64931 - Microbially Promoting Solubilization of Steel Corrosion Products and Fate of Associated Actinides	0	1	0	2

Engineering Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55052 - Advanced Sensing and Control Techniques to Facilitate Semi-Autonomous Decommissioning	0	2	4	0

Inorganic Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54724 - Synthesis of New Water-Soluble Metal-Binding Polymers: Combinatorial Chemistry Approach	0	2	0	0

Materials Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55380 - In-Situ Spectro-Electrochemical Studies of Radionuclide Contaminated Surface Films on Metals and the Mechanism of their Formation and Dissolution	0	0	0	1

59925 - Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems	0	1	0	2
64896 - Decontamination of Radionuclides from Concrete During and After Thermal Treatment	0	1	0	0
64946 - Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic	2	2	1	0
73835(Renewal of Project No.54914) - Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces	0	3	0	2

Separations Chemistry

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
60041 - Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration	0	2	0	1
60283 - Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation	0	0	0	2
64912 - Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners	3	1	0	0
64965 - Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids	0	4	0	0

HEALTH/ECOLOGY/RISK

Analytical Chemistry & Instrumentation

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
60163 - Investigation of Techniques to Improve Continuous Air Monitors Under Conditions of High Dust Loading in Environmental Settings	0	1	0	0

73807(Renewal of Project No.60218) - Rapid Nucleic Acid Analysis for Contaminant Evaluation	0	2	0	0

Biogeochemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
60015 - Long-term Risk from Actinides in the Environment: Modes of Mobility	0	2	0	0

Health/Risk

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54546 - Engineered Antibodies for Monitoring of Polynuclear Aromatic Hydrocarbons	0	3	0	3
54584 - Comparison of the Bioavailability of Elemental Waste Laden Soils Using in vivo and in vitro Analytical Methodology, and Refinement of Exposure/Dose Models	0	0	2	2
54684 - Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup	0	5	0	0
54940 - Improved Risk Estimates for Carbon Tetrachloride	1	0	0	0
55356 - Environmentally-Induced Malignancies: An In Vivo Model to Evaluate the Health Impact of Chemicals in Mixed Waste	0	1	0	0
55410 - Determining Significant Endpoints for Ecological Risk Analysis	0	0	1	1
73942(Renewal of Project No.59918) - Improved Radiation Dosimetry Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites	0	0	0	1

74050(Renewal of Project No.59882) - Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at US DOE Fernald	0	1	0	0

Low Dose Radiation

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
69848 - Adaptive Response Against Spontaneous Neoplastic Transformation in vitro Induced by Ionizing Radiation	1	0	0	0
69906 - Markers of the Low-Dose Radiation Response	0	2	0	3
69938 - Biological Effects of LLIR and Normal Oxidative Damage: The Same or Different?	0	1	0	0
69981 - Mechanisms of Enhanced Cell Killing at Low Doses: Implications for Radiation Risk	0	1	0	0

High-Level Waste

Actinide (Heavy Element) Chemistry

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
54595 - f-Element Ion Chelation in Highly Basic Media	4	5	0	2
59977 - Synthesis and Characterization of Templated Ion Exchange Resins for the Selective Complexation of Actinide Ions	0	4	0	0
73759(Renewal of Project No.54679) - Computational Design of Metal Ion Sequestering Agents	0	3	0	8
81940(Renewal of Project No.65398) - Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leach	0	0	0	2

81962(Renewal of Project No.65352) - Understanding the Chemistry of the Actinides in High Level Waste Tank Systems: The Impact of Temperature on Hydrolysis and Complexation with Organics	1	1	0	2

Analytical Chemistry & Instrumentation

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55318 - Improved Analytical Characterization of Solid Waste Forms by Fundamental Development of Laser Ablation Technology	0	1	0	1
65421 - Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature-Programmed Gas Microsensors	1	1	0	2
81924(Renewal of Project No.60217) - Optical and Microcantilever-Based Sensors for Real-Time In Situ Characterization of High-Level Waste	0	0	0	2
81939(Renewal of Project No.65340) - Hybrid Micro-Electro-Mechanical Systems (MEMS) for Highly Reliable and Selective Characterization of Tank Waste	0	1	4	1

Engineering Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55294 - Superconducting Open-Gradient Magnetic Separation for the Pretreatment of Radioactive or Mixed Waste Vitrification Feeds	12	0	0	0
60143 - Foaming in Radioactive Waste Treatment and Immobilization Processes	0	2	0	1
60451 - Mechanics of Bubbles in Sludges and Slurries	0	0	0	1
65328 - Electrically Driven Technologies for Radioactive Aerosol Abatement	0	3	0	0

65371 - Numerical Modeling of Mixing of Chemically Reacting, Non-Newtonian Slurry for Tank Waste Retrieval	0	1	0	0
73827(Renewal of Project No.54890) - Non-Invasive Diagnostics for Measuring Physical Properties and Processes in High Level Wastes	0	3	0	1

Geochemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
60403 - Phase Chemistry of Tank Sludge Residual Components	0	1	0	0

Geophysics

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55141 - Imaging and Characterizing the Waste Materials Inside an Underground Storage Tank Using Seismic Normal Modes	0	1	0	0

Inorganic Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54628 - Colloidal Agglomerates in Tank Sludge: Impact on Waste Processing	0	0	0	3
54646 - Interfacial Radiolysis Effects in Tank Waste Speciation	0	0	0	3
54765 - Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium, Technetium, and Complexants by Nitrate	4	5	0	1
54807 - Studies Related to Chemical Mechanisms of Gas Formation in Hanford High-Level Nuclear Wastes	0	3	0	0
55137 - Investigation of Novel Electrode Materials for Electrochemically-Based Remediation of High- and Low-Level Mixed Wastes in the DOE Complex	1	2	0	1

73778(Renewal of Project No.60296) - Research Program to Investigate the Fundamental Chemistry of Technetium	0	0	0	1

Materials Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54773 - Microstructural Properties of High-Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies	3	0	0	1
54982 - Analysis of Surface Leaching Processes in Vitrified High-Level Nuclear Wastes Using In-Situ Raman Imaging and Atomistic Modeling	5	0	3	0
73750(Renewal of Project No.54672) - Radiation Effects in Nuclear Waste Materials	0	0	0	5
73976(Renewal of Project No.55110) - Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes	3	0	2	0
81934(Renewal of Project No.60020) - Stability of High-Level Waste Radioactive Waste Forms	0	0	0	1

Separations Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54716 - Polyoxometalates for Radioactive Waste Treatment	1	2	0	2
54996 - Ionizing Radiation Induced Catalysis on Metal Oxide Particles	0	0	0	1
59990 - Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste	0	0	0	1
59993 - Dynamic Effects of Tank Waste Aging on Radionuclide-Complexant Interactions	0	1	0	0

60017 - Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties	0	3	0	0
60050 - Chemical Speciation of Inorganic Compounds under Hydrothermal Conditions	0	3	0	0
60123 - Potential-Modulated Intercalation of Alkali Cations into Metal Hexacyanoferrate Coated Electrodes	2	2	0	0
73803(Renewal of Project No.55087) - Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation	0	1	0	2
73824(Renewal of Project No.59982) - Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation	0	1	0	1
74019(Renewal of Project No.54864) - Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance	0	4	0	0
81912(Renewal of Project No.65409) - Electroactive Materials for Anion Separation - Technetium from Nitrate	0	2	0	0
81935(Renewal of Project No.65339) - Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts	0	2	0	7

MIXED WASTE

Actinide (Heavy Element) Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
60370 - Rational Design of Metal Ion Sequestering Agents	0	3	0	3

Analytical Chemistry & Instrumentation

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55171 - Development of Advanced In Situ Techniques for Chemistry Monitoring and Corrosion Mitigation in SCWO Environments	0	1	0	1
55247 - Ion and Molecule Sensors Using Molecular Recognition in Luminescent, Conductive Polymers	0	1	0	9
60070 - The Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals	0	1	0	0

Engineering Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54973 - A Novel Energy-Efficient Plasma Chemical Process for the Destruction of Volatile Toxic Compounds	0	1	0	1
60326 - Isolation of Metals from Liquid Wastes: Reactive Scavenging in Turbulent Thermal Reactors	0	4	0	0

Inorganic Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54506 - Acid-Base Behavior in Hydrothermal Processing of Wastes	0	1	3	2
54828 - Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water	7	0	0	0
55115 - The Adsorption and Reaction of Halogenated Volatile Organic Compounds (VOCs) on Metal Oxides	0	1	0	3
55276 - Fundamental Chemistry and Thermodynamics of Hydrothermal Oxidation Processes	0	0	0	1

Materials Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55387 - Photooxidation of Organic Waste Using Semiconductor Nanoclusters	0	0	0	2

Separations Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54571 - Removal of Heavy Metals and Organic Contaminants from Aqueous Streams by Novel Filtration Methods	2	0	2	2
54770 - New Anion-Exchange Resins for Improved Separations of Nuclear Materials	0	8	0	2
54847 - Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide	0	0	0	2
54942 - Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO₂	0	3	3	1
55103 - Utilization of Kinetic Isotope Effects for the Concentration of Tritium	0	0	0	2
60096 - Rational Synthesis of Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation	0	6	0	1

NUCLEAR MATERIALS

Analytical Chemistry & Instrumentation

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
60247 - Miniature Nuclear Magnetic Resonance Spectrometer for In-Situ and In-Process Analysis and Monitoring	0	5	0	0

Engineering Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
60077 - Development of Nuclear Analysis Capabilities for DOE Waste Management Activities	0	0	1	0

Materials Science

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
55382 - Determination of Transmutation Effects in Crystalline Waste Forms	0	1	0	1

SPENT NUCLEAR FUEL

Geochemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
73691(Renewal of Project No.59960) - Renewal of Direct Investigations of the Immobilization of Radionuclides in the Alteration Products of Spent Nuclear Fuel	0	3	0	0

SUBSURFACE CONTAMINATION

Actinide (Heavy Element) Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54893 - Research Program to Determine Redox Properties and Their Effects on Speciation and Mobility of Pu in DOE Wastes	0	0	0	4
70035 - DNAPL Surface Chemistry: Its Impact on DNAPL Distribution in the Vadose Zone and its Manipulation to Enhance Remediation	0	4	0	0
70050 - Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone	0	4	0	0
70126 - Collaboration: Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone	0	3	0	0
73819(Renewal of Project No.59996) - Plutonium Speciation, Solubilization, and Migration in Soils	0	1	0	3

Analytical Chemistry & Instrumentation

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54639 - Development of an In-Situ Microsensor for the Measurements of Chromium and Uranium in Groundwater at DOE Sites	1	1	0	0
54698 - Rapid Mass Spectrometric DNA Diagnostics for Assessing Microbial Community Activity During Bioremediation	2	0	0	0
55108 - Monitoring Genetic & Metabolic Potential for In Situ Bioremediation: Mass Spectrometry	0	1	2	1
55205 - A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals	0	7	0	0
55328 - Novel Analytical Techniques Based on an Enhanced Electron Attachment Process	0	1	0	0
70010(Renewal of Project No.54674) - Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone	3	2	7	0
70179 - Radionuclide Sensors for Water Monitoring	0	3	0	0
73808(Renewal of Project No.60197) - Microsensors for In-Situ Chemical, Physical, & Radiological Characterization Mixed Waste	0	5	0	0

Biogeochemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54790 - Microbial Mineral Transformations at the Fe(II)/Fe(III) Redox Boundary for Solid Phase Capture of Strontium and Other Metal/Radionuclide Contaminants	0	3	0	3

55388 - Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents	2	1	0	1
70063(Renewal of Project No.54666) - Biodegradation of Chlorinated Solvents: Reactions Near DNAPL and Enzyme Function	0	3	0	0
70165 - Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation	0	0	2	1
73914(Renewal of Project No.55164) - Reductive Immobilization of U(VI) in Fe(III) Oxide-Reducing Subsurface Sediments: Analysis of Coupled Microbial-Geochemical Processes in Experimental Reactive Transport Systems	0	0	1	1

Engineering Science

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
55211 - Cavitational Hydrothermal Oxidation: A New Remediation Process	0	0	1	1
70045 - Investigation of Pore-Scale Processes which Affect Soil Vapor Extraction	0	2	0	1
70088 - Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone	0	0	0	2
73793(Renewal of Project No.55013) - Biofiltration of Volatile Pollutants: Solubility Effects	0	1	0	0

Geochemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54548 - The Efficacy of Oxidative Coupling for Promoting In-Situ Immobilization of Hydroxylated Aromatics in Contaminated Soil and Sediment Systems	5	3	3	2
54635 - Molecular-Level Process Governing the Interaction of Contaminants with Iron and Manganese Oxides	0	0	2	4
54823 - Modeling of Cation Binding in Hydrated 2:1 Clay Minerals	3	3	0	2
55014 - Kinetics and Mechanisms of Metal Retention/Release in Geochemical Processes in Soil	10	0	1	1
55148 - Hydrologic and Geochemical Controls on the Transport of Radionuclides in Natural Undisturbed Arid Environments as Determined by Accelerator Mass Spectrometry	0	0	0	1
70070 - Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks	0	0	0	1
70081 - Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases	0	7	0	0
70121 - The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments	0	1	0	1
73745(Renewal of Project No.54585) - Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes	0	3	0	2

73775(Renewal of Project No.55396) - Colloid Genesis/Transport and Flow Pathway Alterations Resulting From Interactions of Highly Reactive Waste Solutions and Sediments in the Vadose Zone	0	0	0	2

Geophysics

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54655 - Collaborative Research: Hydrogeological-Geophysical Methods for Subsurface Site Characterization	0	6	0	1
55332 - A Hybrid Hydrologic-Geophysical Inverse Technique for the Assessment and Monitoring of Leachates in the Vadose Zone	0	7	5	3
60162 - Enhancements to & Characterization of the Very Early Time Electromagnetic (VETEM) Prototype Instrument & Applications to Shallow Subsurface Imaging at Sites in the DOE Complex	2	2	0	1
73776(Renewal of Project No.60328) - High Frequency Electromagnetic Impedance Measurements for Characterization, Monitoring, and Verification Efforts	0	0	0	1
70012 - Complex Electrical Resistivity for Monitoring DNAPL Contamination	0	1	0	0
70052 - Material Property Estimation for Direct Detection of DNAPL Using Integrated Ground-Penetrating Radar Velocity, Imaging, and Attribute Analysis	0	1	0	0
70108(Renewal of Project No.55411) - Effects of Fluid Distribution on Measured Geophysical Properties for Partially Saturated, Shallow Subsurface Conditions	3	1	0	0
70115(Renewal of Project No.54699) - The Use of Radar Methods to Determine Moisture Content in the Vadose Zone	0	2	1	1

73731(Renewal of Project No.60199) - Automating Shallow Seismic Imaging	0	3	0	0
73830(Renewal of Project No.55218) - Seismic Surface-Wave Tomography of Waste Sites	3	0	0	2
73962(Renewal of Project No.60115) - Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface	0	2	0	0

Health/Risk

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
55033 - Characterization of Chemically Modified Hyperthermophilic Enzymes for Chemical Syntheses and Bioremediation Reactions	0	0	1	5

Hydrogeology

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
54576 - On the Inclusion of the Interfacial Area Between Phases in the Physical and Mathematical Description of Subsurface Multiphase Flow	0	0	0	2
54888 - Manipulating Subsurface Colloids to Enhance Cleanups of DOE Waste	0	2	0	1
55036 - Colloid Transport and Retention in Fractured Deposits	0	5	0	1
55083 - Behavior of Dense, Immiscible Solvents in Fractured Clay-Rich Soils	0	4	1	0
55359 - Chaotic-Dynamical Conceptual Model to Describe Fluid Flow and Contaminant Transport in a Fractured Vadose Zone	7	2	2	1

70135 - Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone	0	3	0	1
70149(Renewal of Project No.54950) - The Dynamics of Vadose Zone Transport: A Field and Modeling Study Using the Vadose Zone Observatory	0	0	0	1
70187 - Quantifying Vadose Zone Flow and Transport Uncertainties Using a Unified, Hierarchical Approach	0	0	0	1
73732(Renewal of Project No.54680) - Migration and Entrapment of DNAPLs in Heterogeneous Systems: Impact of Waste and Porous Medium Composition	1	2	4	0
73812(Renewal of Project No.55395) - Physics of DNAPL Migrations and Remediation in the Presence of Heterogeneities	3	0	1	0

Inorganic Chemistry

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
55061 - Fundamental Studies of the Removal of Contaminants from Ground and Waste Waters via Reduction by Zero-Valent Metals	0	6	0	0
55119 - Phase Equilibria Modification by Electric Fields	1	1	3	2

Microbial Science

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
54681 - Dynamics of Coupled Contaminant and Microbial Transport in Heterogeneous Porous Media	0	3	0	2
55031 - Genetic Analysis of Stress Responses in Soil Bacteria for Enhanced Bioremediation of Mixed Contaminants	2	1	0	2

55105 - Complete Detoxification of Short Chain Chlorinated Aliphatics: Isolation of Halorespiring Organisms and Biochemical Studies of the Dehalogenating Enzyme Systems	0	1	0	0
55416 - Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media	0	0	3	2
59786 - Design and Construction of *Deinococcus radiodurans* for Biodegradation of Organic Toxins at Radioactive DOE Waste Sites	0	1	1	2

Plant Science

Project Number & Title	*Undergrads*	*Masters*	*Ph.D.s*	*Post Docs*
55097 - Heavy Metal Pumps in Plants	0	0	1	0
55278 - Molecular Genetics of Metal Detoxification: Prospects for Phytoremediation	0	0	1	4
60271 - Characterization of a New Family of Metal Transport Proteins	0	3	0	0
70054(Renewal of Project No.54837) - Phytoremediation of Ionic and Methyl Mercury Pollution	0	4	0	1
73843(Renewal of Project No.55118) - Mechanisms of Heavy Metal Sequestration in Soils: Plant-Microbe Interactions and Organic Matter Aging	0	0	0	3
73858(Renewal of Project No.54889) - Chlorinated Hydrocarbon Degradation in Plants: Mechanisms and Enhancement of Phytoremediation of Groundwater Contamination	0	2	0	2

Separations Chemistry

Project Number & Title	Undergrads	Masters	Ph.D.s	Post Docs
54122 - A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water By Deep Oxidation	0	2	0	1

EMSP Researcher works with a trickling biofilter that removes dulite organics for contaminated air streams. [see Project #73793, renewal of #55013]

Phase equilibria and interfacial transport may be modified to enhance separations by applying an electric field. A vapor-liquid-equilibrium experiment is shown here. [see Project #55119]

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TOPICAL WORKSHOPS

Workshops and other interactive forums sponsored by the EM Science and Risk Policy Programs are useful research integration tools because they bring researchers and technology users together. EMSP workshops either center on subject-specific or site-specific topics, using a particular theme to highlight pressing problems within EM, or are held in conjunction with Focus Area reviews and professional society meetings. The objective of tying an EMSP workshop to a Focus Area review is to better define end-user needs so researchers fully understand the site problem for which their research is targeted. Workshops typically feature presentations of the research being conducted by the principal investigators, with industry and/or end-user participation and feedback.

The EMSP Process Relative to the Focus Areas

Such forums allow the EMSP researchers to learn about and discuss actual technology needs with the end-users. At the same time, site representatives and other end-users have an opportunity to hear about science developments directly from those conducting the R&D work. The EM/OST Focus Areas provide the linkage between the EMSP projects and the Department's ongoing waste management and clean-up programs within the Offices of Waste Management (EM-30), Environmental Restoration (EM-40), and Nuclear Materials and Facility Stabilization (EM-60). The five Focus Areas OST currently supports are:

- Deactivation and Decommissioning Focus Area (DDFA)
- Mixed Waste Focus Area (MWFA)
- Nuclear Materials Focus Area (NMFA)
- Subsurface Contaminants Focus Area (SCFA)
- Tanks Focus Area (TFA).

Through communication and cooperation between EM's site end-users, the Focus Areas identify opportunities to integrate the research results of EMSP projects to improve performance and reliability of their baseline clean-up technologies. The Focus Areas also evaluate EMSP projects and results to reveal opportunities to develop breakthrough technologies to solve EM's long-term environmental problems and reduce risk. Figure 1 shows the circular flow of information between the EMSP and the Focus Areas.

Moving research results to application by end-users involves:

- Working with DOE problem holders to identify needs and priorities
- Working with the OST Focus Areas to coordinate activities
- Communicating science results to Focus Area technology developers and EM problem holders.

Dialogue between the end-users and the researchers regarding how the research results can be applied enables sufficient customer understanding of the EMSP projects to "pull" technology down the chain from research to deployment. Focus Areas indicate and facilitate interaction where there is a potential application and provide recommendations for tailoring planned research activities towards Focus Area needs.

The workshops have been very successful and the presentations made by the researchers have been of consistently high quality. Details of the past and planned workshops, including presentations, are available on our program web page (http://emsp.em.doe.gov/workshops/index.htm).

Workshop on Integration of End-user needs with Research Projects for EMSP
July 9-10, 1998
Savannah River Site, SC

The purposes of this workshop were to inform EMSP principal investigators of environmental restoration program needs at SRS, to inform the end-users of currently funded EMSP projects that have relevance to SRS needs, and to determine and plan a program to meet gaps and unmet needs using EMSP research. Among the seventy-five representatives in attendance were EMSP principal investigators; STCG and SCFA end-users; scientists from regional universities, including minority serving institutions and university consortia; DOE contributors; and M&I contractors. The workshop participants received overviews of EMSP and SCFA technologies currently in use at SRS, as well as SRS end-user needs and STCG activities. Tours were available for workshop participants to see SRS needs first-hand.

Three subgroups were formed to develop deployment plans for (1) phytoremediation, (2) DNAPL, characterization, and bioremediation, and (3) metals and rads. The outcome of the phytoremediation subgroup was extremely successful in providing an abbreviated deployment project plan. It was concluded that phytoremediation was a viable technology to meet two stated needs: (1) deploy passive technology for attenuation of VOC, and (2) utilize innovative technologies to replace pump and treat technology. The subgroup proposed three phytoremediation pilot scale demonstrations utilizing loblolly pines, poplar trees, and an aquatic lagoon system. Timelines and cost estimates to process the projects from the science phase through deployment were developed. The DNAPL, characterization, and bioremediation subgroup was less optimistic about the application of the selected southeastern science projects to SRS needs. SRS has large DNAPL plumes where characterization is needed and improved off-gas treatment from vapor extraction technologies is desirable. These selected projects address a gap at SRS. The technologies are 5-9 years away from deployment and currently available technologies allow cleanup to progress. The metals and rads subgroup directed the participating PIs towards discussions with high level waste end-users.

First Environmental Management Science Program National Workshop July 27-30, 1998 Chicago, IL

The first Environmental Management Science Program (EMSP) National Workshop was held July 27-30, 1998 to communicate the progress and plans of all then-active projects. It served as an opportunity for scientists in different disciplines across the program to become acquainted with each other, and to discuss and coordinate research plans. Abstracts for those projects are available in CD-ROM and hardcopy formats and can also be accessed from the EMSP web site at ***http://emsp.em.doe.gov***. The EMSP web site also provides up to date information about ongoing research projects, future events, updated technology needs, and links to other related environmental R&D programs.

INEEL Science Integration Workshop
October 20-22, 1998
Idaho Falls, ID

This site-specific workshop included 101 attendees with interests in four science areas: fractured rock, high level waste (calcine separations), decontamination and decommissioning (D&D), and LandTech. Fractured rock sessions included 12 presentations of ongoing research, followed by two working sessions to discuss opportunities for increased collaboration, as well as the identification of science and technology gaps related to understanding and remediating contaminated fractured rock environments. The D&D group toured the sewage treatment facility at CFA, Pit 9, and the nuclear airplane engine exhibit. The high level waste group toured the calcining facility at INTEC. The LandTech group developed a set of research requirements during their breakout session, and also toured Box Canyon.

Interactions between the PIs and end-users included the following:

- Application of "Lab on a Chip" where Brad Frazee (INEEL) and Greg Collins (Naval Research Laboratory) discussed needs characterization information concerning their important constituents. It was decided that (1) Tom Thiel would get information on the top twelve hitters of "Lab on a Chip" to Greg Collins; (2) Greg would contact the INEEL Sample Management Office in order to test the samples; (3) large scale demonstration of "Lab on a Chip" would be done by Greg and Dick Meservey; and (4) Greg would keep Dick apprised on further research done, with the goal to be using the "Lab on a chip" in the field as part of a large scale demonstration project.

- Mike Savina and Maurice Ross of TRA met with Zawtech, Inc. while in Idaho Falls and they are discussing CRADAs and other industrial partnerships regarding Laser Ablation and Robotics for scabbling.

- Information from INEEL requested transfer of knowledge regarding D&D cost estimates from Brad Frazee. Completed by providing the researchers with the URL that has the information on it.

- Brad Frazee and Dick Meservey will track progress of a novel class of sensors based on light diffraction utilizing polymerized colloidal crystalline arrays for longer-term usage (Sanford Asher). DDFA is interested in field testing a portable sensor.

- Inorganic Ion Exchange Materials for Environmental Restoration research is a promising area because there is an increasing concern regarding water treatment as the size of the reactor being decontaminated and decommissioned increases. The end-users believe there will be a need in the future as commercial power plants are decommissioned. Full-scale membrane filters are needed to cleanup fuel storage basins at the INEEL to warm waste pond disposal limits.

Workshop on Integration of End-user needs with Research Projects for EMSP Focus on Deactivation and Decommissioning November 17-18, 1998 Savannah River Site, SC

The purposes of the workshop were to:

- Increase the awareness of the EMSP principal investigators of the role of the DDFA and thereby increase the applicability of their projects to the D&D mission of DOE
- Improve SRS knowledge of the EMSP research
- Identify EMSP projects that have direct usefulness to SRS D&D activities
- Determine and discuss EMSP project needs.

Twenty principal investigators and 31 individuals representing the DDFA, end-users, scientists, and DOE program representatives listened to overviews of the EMSP program and the DDFA, discussed lessons learned from the D&D breakout session at the INEEL Workshop and results from the D&D Large Scale Demonstration at the INEEL, and toured SRS's D&D Large Scale Demonstration. The EMSP principal investigators provided a short overview of their projects and afterwards hosted a poster session.

The EMSP PIs gained an improved knowledge of the D&D needs of DOE as a result of the workshop. SRS and selected segments of the DOE complex were informed of the EMSP D&D related research. SRS will provide mentors to several of the projects. Fourteen PIs identified current needs to increase the effectiveness of their research projects. These needs include:

- Representative samples that can be used to test the decontamination process being developed in the laboratory. (A.J. Francis)

- Replicate contaminated metal coupon for quantitative lab tests on biological coatings for removal of contamination radiation. Need to know what is considered "fixed contamination". (Brian Davison)

- Monitoring of mixtures of radionuclides and examining actual samples (e.g. concrete drill samples). Field testing to compare to baseline technologies. (Greg Collins)

- Concrete surface samples and priority of contaminants on concrete (particularly radionuclides). (Brian Spalding)

- Indoor/outdoor location with radioactive airborne contamination to test sampling equipment. Identification of industrial partners. (Piotr Wasiolek)

- More information of the structure and composition of surface contaminants to enable design of more realistic experiments. (Steve Babayan)

- Composition of radioactively contaminated surface layers on pipes and storage tanks, (i.e., type of radionuclides, heavy metal ions, etc.), level of contamination, thickness of surface film. Need 2" x 2" samples. (Carlos Melendres)

- Information on general residues (organics/inorganics/particulates). (R.M. Counce)

- End-users that could benefit from: (1) predictive capability of diffusion between contaminants (plutonium, uranium, etc.) and metal they are in contact with/ contained by (e.g., glove box components and steel storage containers), and (2) a mobile apparatus to detect degree of contamination, chemical and physical characterization of contaminant that has been painted over as opposed to being in a steel container. (Bernard Cooper)

- Database of: (1) alloys/metals commonly contaminated, (2) atmospheric conditions of typical storage and operation in D&D facilities, (3) typical paints/surface coatings that are found on these surfaces, and (4) method and length of time of contamination or exposure to contaminants. (Gary Halada)

These needs range from common samples that could be decontaminated to a mini demonstration facility where representative radioactive samples could be decontaminated with prototype equipment to evaluate the prototype before proceeding to the large scale demonstration facilities provided by the DDFA. Many of the university PIs do not have licenses or facilities to handle radioactive materials, yet need access to these materials for their research.

Tanks Focus Area (TFA) Workshop
November 17-18, 1998
Richland, WA

The Tanks Focus Area (TFA) develops technologies to safely and efficiently remediate radioactive waste stored in underground tanks at four sites nationwide. This work is done by leveraging resources and working with a broad team of experts from industry, national laboratories, government contractors, universities, stakeholders, and U.S. Department of Energy.

The goal of the workshop was to further collaboration between EMSP researchers and TFA end-users in the areas of tank waste characterization, retrieval and pretreatment, and tanks remediation. TFA needs were conveyed to the researchers and interactions were established to transfer the research results to the end-user. Linkage to new and past TFA needs and points of contact were given. EMSP awardees discussed their research plans and received feedback from TFA Technical Integration Managers and safety personnel. Minutes from the breakout sessions summarize TFA questions, recommendations to the researchers, linkages to related tasks, and points of contact.

- *Detection and Characterization of Chemicals Present in Tank Waste* by Dr. P. G. Datskos* (ORNL) and Dr. Sepaniak (Univ. of Tenn.)

  Questions:
  - How do you keep the sensor clean?
  - What is the effect of the tank contents (i.e., caustic, acidic, etc.) on the coating?
  - Is there an upper limit for temperatures?
  - How does radioactivity effect the electronics?

  TFA Recommendation:
  - There is a need for at-tank rather than in-tank characterization.
  - Look at organics at low-levels (ppm) rather than bulk constituents.
  - Look at suitable analytes.

- *Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature Programmed Gas Microsensors* by Dr. Semancik & Dr. Tarlov (NIST), Dr. McAvoy & Dr. Suehle (U of Maryland) - presented by Richard Cavicchi (NIST)

  Questions:
  - Is it reversible?
  - Can it be made quantitative?
  - What are the levels of detection?

  TFA Recommendation:
  - No site needs submitted to TFA for tank head-space monitor development in 1995-1998 time period. 8/95 discussions with Hanford project manager for head space gas analysis in tank SY101 indicated that WHC was satisfied with

IR, GC, & H_2 chemical cell monitoring of the vent off-gas. CMST pursued the question of in-tank head-space H_2 monitoring with the TFA in 5/96 and found no apparent need at Hanford.

– There is a potential application for this technology in the Mixed Waste Focus Area for incinerator off-gas monitoring.

- *Mass Spectrometric Fingerprinting of Tank Waste Using Tunable Ultrafast Infrared Lasers* by Dr. Haglund (Vanderbilt University) and Dr. Wayne Hess (PNNL)

  Questions:
  – Can it be made quantitative?

  TFA Recommendation:
  – The usefulness of this tool is for quantitative (molecular species) measurements of organics in solids.

- *Electrically Driven Technologies for Radioactive Aerosol Abatement* by O.A. Ezekoye (University of Texas)

  – No linkage found within the TFA.
  – Potential end-users of this technology might be found in the following areas: calcine off-gas, vitrification, and spent nuclear fuel.
  – Other potential applications, such as medical applications, might be found by reviewing the proceedings of the Nuclear Air Cleaning Conference.

- *Precipitation and Disposition of Aluminum-Containing Phases in Tank Waste* presented by Jun Liu representing the collaboration of Baskron, Virden, Wang, and Keefer from PNNL with Hobbs from SRTC and with Dabbs and Aksay from Princeton.

  The TFA asked Jun if he could/would analyze a specimen of the 101 SY tank crust, if he had it. The TFA, Randy Kirkbride, Andy Felmy, and Jun engaged in a discussion about the ability to get this data into the form of information that could be used in the ESP model.

- *Solution Effects on Cesium Complexation with Calixerene Crown Ethers from Liquid to Supercritical Fluids* presented by Chien Wai of the University of Idaho.

  Most of the subsequent discussion centered on the viability of a process that operates at 75 atmospheres in a nuclear environment. This concern has hampered efforts to employ this type of technology in other waste management arenas such as mixed waste. The TFA contends that it is not likely to pass the safety analysis reviews in the foreseeable future. Chien Wai indicated that he would refocus the program to use his experiments to elucidate dissolution mechanisms.

- *Graduate Students* was presented by Yasuo Onishi (PNNL) representing a large number of collaborators: Felmy, Rustad, Recknagle, Michener, Fann (PNNL); Jordon (IBM); Liu (CRAY-SGI Research); and Yuen (University of Minnesota).

TFA asked if differing tank geometries could be included in the model and was reassured that this was the case. TFA indicated that they had funded some tank settling tests for C-106, C-107, and S-106 and would like this data to be used in the model. TFA indicated a desire to have Onishi collaborate with Florida International University in their upcoming line plugging tests.

Characterization, Monitoring and Sensor Technology Crosscutting Program (CMST-CP) Annual Review March 8-11, 1999 Gaithersburg, MD

Thirty-three people attended the EMSP Presentations during the CMST-CP Annual Review. Eighteen attendees were associated with the EMSP and 15 others were from CMST-CP, Focus Areas (FAs), the Nuclear Regulatory Commission, and FETC. There was much interest in the EMSP research by CMST and the FAs.

Eleven EMSP projects and one Wolf-Broido project were presented. There were four research projects on the subject of laser ablation — the researchers were knowledgeable about what the other researchers were doing in the area and formed their own collaborations. A fact sheet describing each project scheduled for presentations was prepared for each EMSP presenter and made available to the CMST-CP Review prior to the presentations. The FA/CP personnel read the information on the fact sheets prior to the EMSP presentations so that they would have some background on the projects and could decide which presentations they wanted to attend. Boris Fabyschenko from LBL distributed a press release on the application of chaos theory to fractured media. Andrew Pipino from NIST displayed a poster on the Evanescent Wave Cavity Ring-Down Miniature Spectrometer in the back of the meeting room. Mark Pickrell from LANL addressed transfer of his mature research project, which has developed a neutron source; two commercial partners have subsequently applied for a license. Four laser ablation research projects were presented (Rick Russo, Scott Goode, Mike Anderson, and Mike Pellin) and CMST expressed interest in perhaps integrating these projects into a follow-on technology development effort.

The banquet was well attended (28 people) and there was a lot of interchange during dinner. The reception afterwards at the hotel provided an opportunity to meet with the researchers and learn more about how to transition their research.

The Environmental Measurements Laboratory (EML) visit was informative and a good opportunity to get to know the DOE/NV CMST manager, the EML personnel, and EMSP researchers and learn about the research conducted by EML. EML will be performing quality assessments and project facilitation for CMST. Close contact between the CMST PIs and the project facilitators keeps the CMST projects on track and aligned with FA/Crosscut needs.

Subsurface Contaminants Focus Area (SCFA) Mid-Year Review
April 26-29, 1999
Augusta, GA

An EMSP room was set-up and over 20 PIs presented posters of their vadose zone work. The poster sessions were well attended. PIs had the opportunity to attend presentations by site personnel discussing current vadose zone cleanup activities.

A special session was held for PIs that was attended by the program manager of the EMSP, Mark Gilbertson, and Tom Hicks from SCFA. Discussions centered around general project descriptions, the SCFA path forward for incorporating EMSP projects in the Focus Area, and PI feedback to Mark Gilbertson. Several of the PIs voiced their support of the recent EMSP research integration efforts including the topical workshops and participation with the Focus Areas.

Deactivation and Decommissioning Focus Area (DDFA) Mid-Year Review May 25-27, 1999 Morgantown, WV

At the request of the DDFA, the Environmental Management Science Program (EMSP) attended and participated in the DDFA Mid-Year Review. Chester Miller of the DOE-HQ made presentations for 21 of the 22 EMSP projects related to DDFA. Dr. Bernard Cooper of the University of West Virginia attended and presented his project. Posters for 8 EMSP DDFA related projects were displayed.

Dr. Cooper indicated that his project is now at a point that he needs someone as a "broker" to help progress it to the next step. He feels that the next step will be to perform field-testing. He is also interested in testing his methods on plutonium/ uranium samples.

Dr. William Stone of NIST expressed interest in Dr. George Xu's presentation on "Real-Time Identification and Characterization of Asbestos and Concrete Materials with Radioactive Contamination". He was provided with a copy of Dr. Xu's presentations, poster and contact information.

The EMSP Staff met with Robert Vagnetti from the DDFA to establish a dialogue on how the EMSP could best support the DDFA in the future and how to make our gap analyses more useful. Mr. Vagnetti indicated that he would be willing to review our current gap analysis and help in efforts for possible research integration.

American Chemical Society (ACS)
August 22-26, 1999
New Orleans, LA

The EMSP will have a strong presence at the ACS Meeting with 120 presentations in 8 technical sessions dedicated to EMSP projects. There will also be 2 tutorials, a plenary session, and 2 poster sessions. A poster on research integration for the EMSP will be presented by EMSP staff. This will provide a forum for researcher interaction among EMSP researchers and non-EMSP funded researchers. A large fraction of the EMSP portfolio addresses research that deals with actinide chemistry issues faced by DOE.

Oak Ridge Operations Environmental Management Science Program Workshop September 22, 1999 Oak Ridge, TN

The purposes of this workshop were to inform EMSP principal investigators of the Oak Operations Office's (ORO) environmental cleanup needs, introduce end-users to EMSP projects that have relevance to ORO needs, and to cultivate collaborations and other relationships between the participants. More than seventy attendees participated in the workshop, including: EMSP researchers; representatives from the Site Technology Coordination Group, Subsurface Contaminants Focus Area, state regulators, and public stakeholder groups; end-users from the major sites administered by the Oak Operations Office; and EMSP staff.

The day's activities began with a short bus tour of two of the three sites that encompass the Oak Ridge Reservation (ORR), the East Tennessee Technology Park and Y-12 Site. The group reconvened at the conference center for a warm Tennessee welcome by the Oak Ridge Operations Office, an introduction to the EMSP, and presentations by the various end-users about their site problems. The sites discussed included the Paducah Gaseous Diffusion Plant, the Portsmouth Gaseous Diffusion Plant, the Y-12 Site, the Oak Ridge National Laboratory (ORNL), and the East Tennessee Technology Park (ETTP, formerly the K-25 Site). After lunch, the participants were guided into one of four breakout sessions where researchers presented their work and discussions about how it related to site needs ensued. The breakout session topics were: 1) D&D Characterization, Decontamination, and Recycle; 2) Soil and Groundwater Treatment; 3) Subsurface Imaging and Characterization; and 4) Bioremediation. Researchers were selected to present their work based on their project's relevancy to ORO cleanup needs.

Interactions between PIs and end-users included the following:

- Dr. A. J. Francis (Brookhaven National Laboratory) and Dr. Gary Halada (SUNY at Stony Brook) began discussions with Gary Person about testing their D&D techniques on materials at ETTP. Their project is titled "Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces."

- Dr. Sherman Ponder started discussions with Jerry Harness, representing the Efficient Separations Crosscutting Program, about possible use of Dr. Ponder's unique separations technology. Dr. Ponder's project is titled "Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties."

- Dr. Ernest Majer's presentation, "Subsurface High Resolution Definition Of Subsurface Heterogeniety For Understanding The Biodynamics Of Natural Field Systems: Advancing The Ability For Scaling To Field

Conditions", sparked interest by the Subsurface Contaminants Focus Area DNAPLs Product Line Manager, Elizabeth Phillips. They will continue discussions in an effort to collaborate in the future on some bioremediation work.

The site tour generated further interest in seeing more detail about ORNL's subsurface contamination and decontamination and decommissioning projects. A follow-on tour is now being arranged for ORNL principal investigators to meet with team leads for these projects.

Nuclear Materials Focus Area EMSP Actinide Chemistry Workshop
November 9-10, 1999
Albuquerque, NM

This workshop brought EMSP principal investigators in contact with representatives and researchers from the Nuclear Materials Focus Area, Nuclear Materials Lead Laboratory, Seaborg Institute, and the Plutonium Center. Research presented during this two-day workshop was designed to highlight current activities related to actinide chemistry of plutonium stabilization, actinides in the subsurface, and actinides solution separations.

Twelve EMSP oral presentations were made, and approximately 20 posters were displayed representing other EMSP research. Topical sessions included in this workshop were:

- Program Overviews
- Clean-up/Decontamination Methods
- Behavior in Groundwater and Soils
- Actinide Behavior in High-level and Other Wastes
- Surveillance, Monitoring, Characterization, and Sensor Development
- Actinide Separations Chemistry and Techniques.

The workshop was attended by more than 40 registered individuals, and due to the close proximity with Sandia National Laboratory, Los Alamos National Laboratory, and The University of New Mexico, numerous non-registered attendees came to selected sessions. As an added activity, attendees were given the opportunity to comment on the EMSP program. At least 10 specific action items were recommended for program improvement.

The workshop ended on a positive note with all participants agreeing that meetings of this type were beneficial and provided opportunities for information exchange related to program needs and areas of promising research and technology development.

Kickoff Workshop for the 1999 Environmental Management Science Program Vadose Zone Research Awards November 16-18, 1999 Richland, WA

These proceedings document the Kickoff Workshop for the 1999 Environmental Management Science Program Vadose Zone Research Awards. The workshop attendees were comprised of researchers, Focus Area representatives, EMSP staff, and science and technology endusers. Three integration teams were formed: (1) Waste/Sediment Lab Experiments and Process Models, (2) Vadose Zone Transport Field Studies, Advanced Characterization, and Transport Modeling, and (3) Monitoring and Remediation at Hanford and Across the Complex. The researchers had the opportunity to listen to talks given by Focus Area representatives, EMSP staff, and science and technology endusers and to present their proposed research plans. The purpose of holding the workshop at the outset of the award process is to give the PIs critical information necessary to direct their research towards the most useful avenues, make available existing data and models, involve the PIs in plans for future vadose zone activities, encourage collaboration among researchers and with endusers, and provide feedback to maximize the benefit of the research. The nucleus of each of these three integration teams will be kept intact through a series of follow-on workshops.

Second Environmental Management Science Program National Workshop April 24-28, 2000 Atlanta, GA

The second Environmental Management Science Program (EMSP) National Workshop was held in Atlanta, GA, from April 24-28, 2000, in order to capitalize on Department of Energy (DOE) investments in environmental science and technology by bringing together environmental management-targeted basic research scientists with Environmental Management Focus Area personnel, site end users, private industry, and other interested parties. EMSP chose the theme *"Science Advancing Solutions"* for this workshop to underscore its commitment to transferring EMSP research results to other Office of Science and Technology programs for further development and ultimate deployment.

The National Workshop brought EMSP Principal Investigators (PIs) together to allow scientists to showcase their research to other scientists, thereby facilitating research synergy. PIs also had the opportunity to meet and interact with DOE site operations and other related Environmental Management Office of Science and Technology (OST) programs personnel (e.g., Focus Areas and Cross-cutting Programs).

The National Workshop was structured with an opening plenary session, followed by breakout sessions, poster sessions, and closing plenary sessions for breakout session summaries and closing remarks. A tour of the Savannah River Site was offered as part of the National Workshop. As a side benefit, a training course on Monitored Natural Attenuation was sponsored by EMSP and presented by the DOE National Environmental Training Office.

One of the most significant goals of the National Workshop was to create research integration opportunities. To achieve this goal, breakout sessions were coordinated and conducted with the Focus Areas and other related programs. The following breakout sessions were conducted:

- Deactivation and Decommissioning Focus Area
- Mixed Waste Focus Area
- National Spent Nuclear Fuel Program
- Nuclear Materials Focus Area
- Subsurface Contaminants Focus Area
- Tanks Focus Area
- Long Term Stewardship
- Low Dose and Risk
- CRESP

Each session chairperson set the agenda for their respective breakout session. Session chairpersons reviewed the EMSP project portfolio, and identified specific projects that contained relevant research with the highest potential for technology development activities. The session chairpersons invited PIs from those projects to present their research to the potential end-users and other PIs.

Sensor Initiative Workshop
June 19-20, 2000
Idaho Falls, ID

A workshop co-sponsored by the Environmental Management Science Program (EMSP) and Long-term stewardship Program was held at the Idaho National Engineering and Environmental Laboratory (INEEL) on June 19 and 20, 2000. The goal of the workshop was to identify research opportunities for sensor development for long-term stewardship. The workshop involved participation, both at the INEEL and via televideo links, by INEEL, Argonne National Laboratory (ANL-West and ANL-East), Fernald, Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), Paducah, Portsmouth, the Savannah River Site (SRS), Sandia National Laboratories (SNL), Nevada, the CMST crosscutting program, and researchers representing twelve EMSP projects. Sensor needs for monitoring and validation applications were identified, functional requirements for the sensors were specified, national laboratory and EMSP research and capabilities were presented, and opportunities for collaboration between the national labs and the EMSP were assessed. The workshop participants agreed to have subject matter experts at their respective sites review and validate the information contained in this report. An overwhelming concensus recommended that a working group be formed to address sensor requirements for long-term stewardship and participate in the roadmap development.