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.

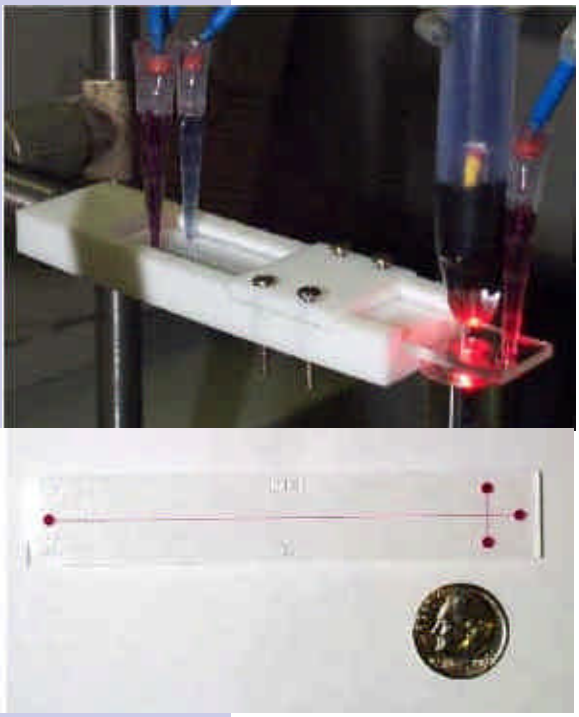
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: John Jones and Bruce Crow
Collaborating Organization: DOE-NV

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.



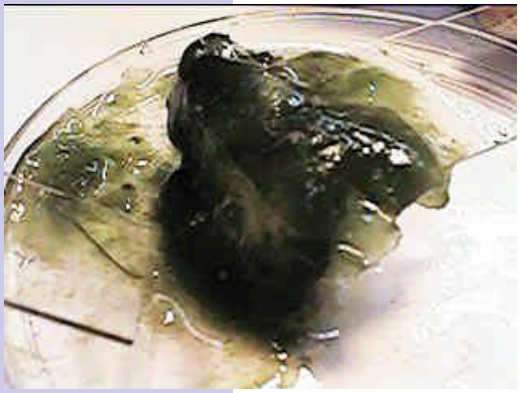
The portable Lab-on-a-Chip Sensor for Radionuclide and Heavy Metals is intended to provide a field portable characterization instrument for in-situ waste characterization. [see Project #82749, renewal of #64982]

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

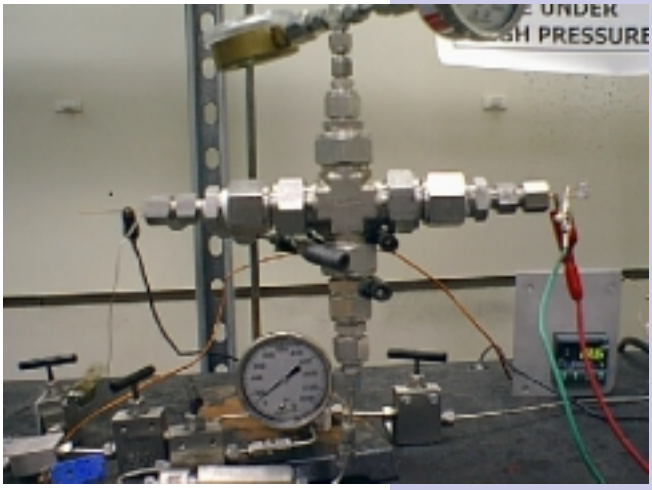
Description: The researchers for this project identified an end-user and began collaborations with the INEEL Decontamination, Decommissioning, and Remediation Optimal Planning System (DDROPS). The INEEL system has widespread applicability throughout DOE and is leading edge technology estimated to save 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.

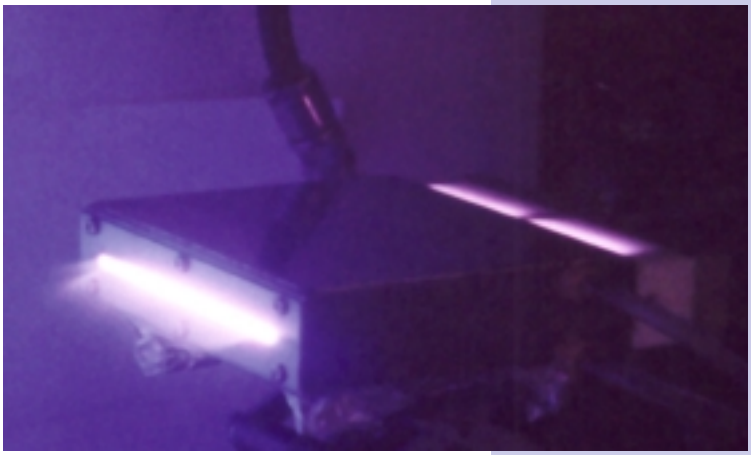
Collaboration Type: Program interaction *Fiscal Year:* 2000
Collaborator: Mark Argyle
Collaborating Organization: INEEL

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.

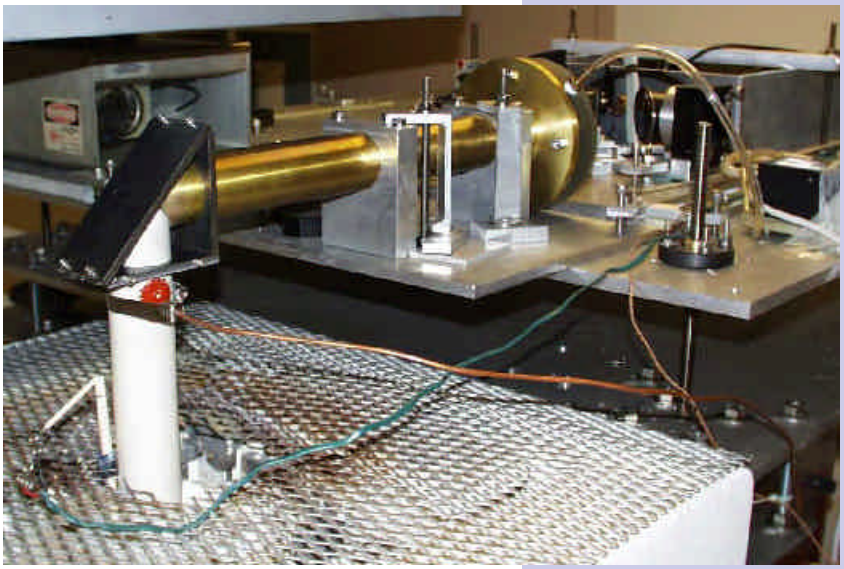
Collaboration Type: Joint interaction *Fiscal Year:* 2001
Collaborator: Bill Holtzcheiter, Frank Thomas III, from SRTC; Tom Thomas, from INEEL; Glenn Bastiaans, from Ames; S. K.. Sundaram, from PNNL
Collaborating Organization: Tanks Focus Area

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

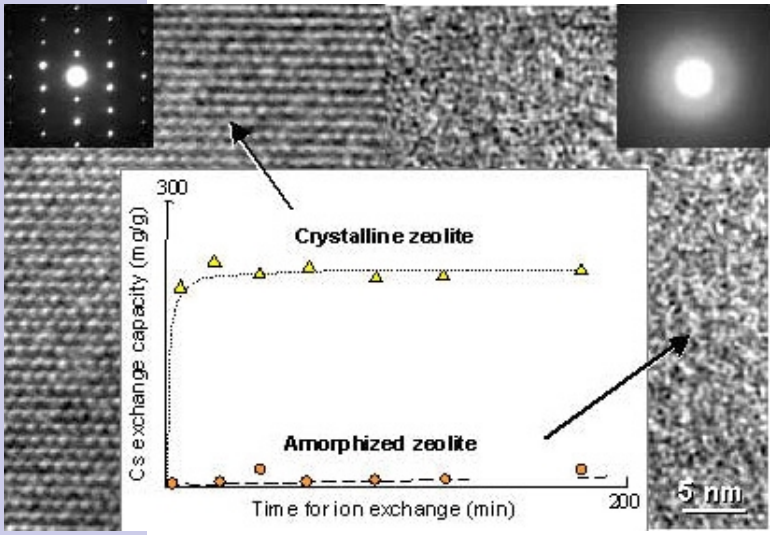
- We have obtained silicotitanate samples synthesized by Prof. Clearfield and conducted a preliminary study on radiation effects in the sample.

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

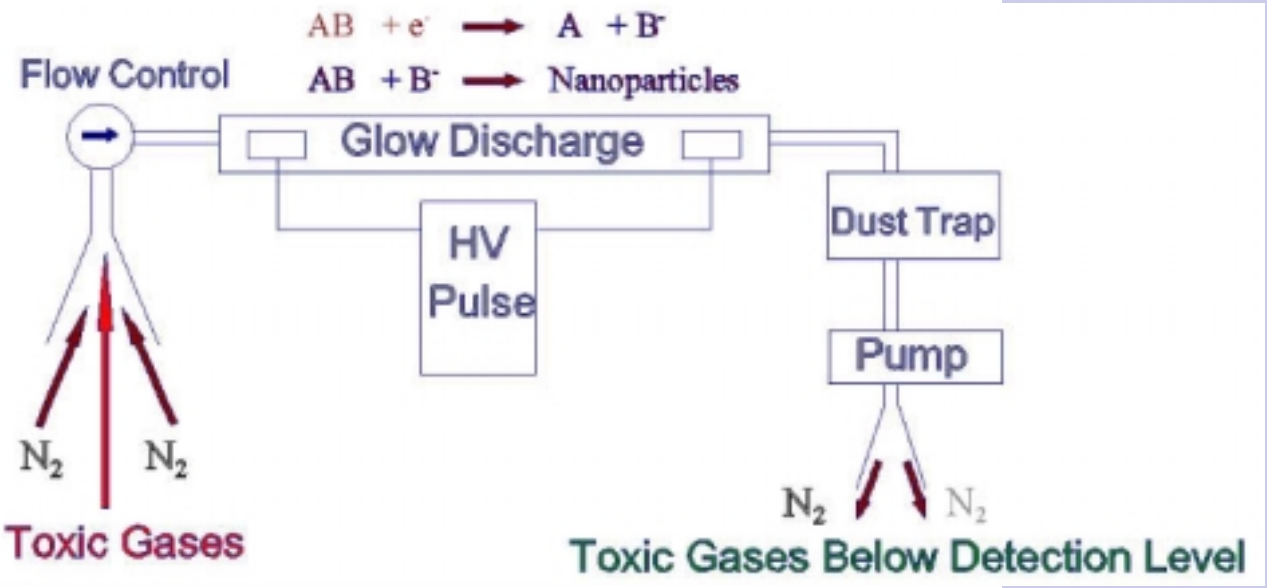
Engineering Science

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

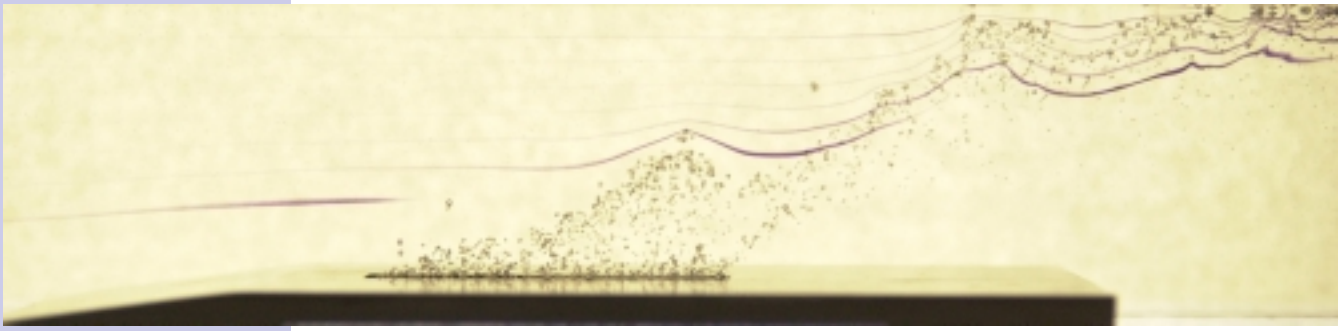
SPENT NUCLEAR FUEL

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,

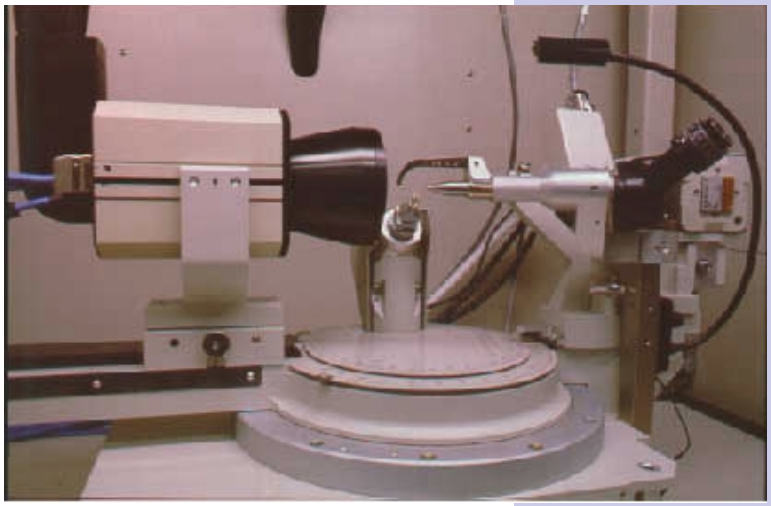
designed the experiments conducted. The SNF staffs have provided understanding of needs for fundamental studies and have reviewed project results and plans for our fundamental studies.

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

Geochemistry

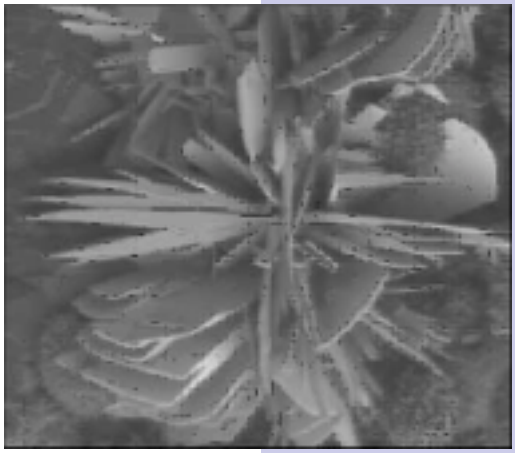
Project: 73691 (Renewal of Project 59960)

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.

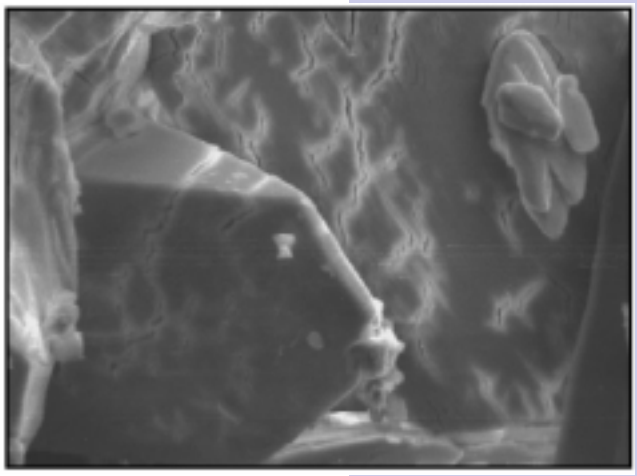
Collaboration Type: Program interaction *Fiscal Year:* 2001
Collaborator: Dr. Lynda Soderholm
Collaborating Organization: Argonne National Laboratories

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

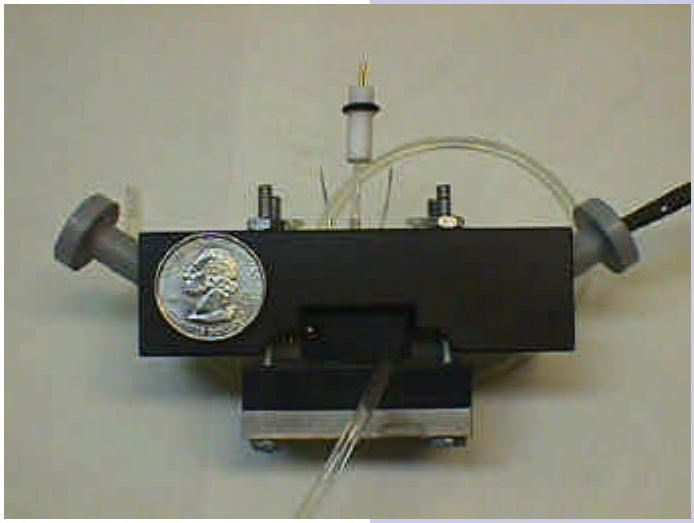
Description: Several DOE sites have been contaminated by transuranic radionuclides (TRU). Manganese oxide/hydroxide minerals, present as minor phases in the vadose zone, can preferentially sequester TRU over iron oxides and other minerals present in much larger quantities. In order to understand the 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).

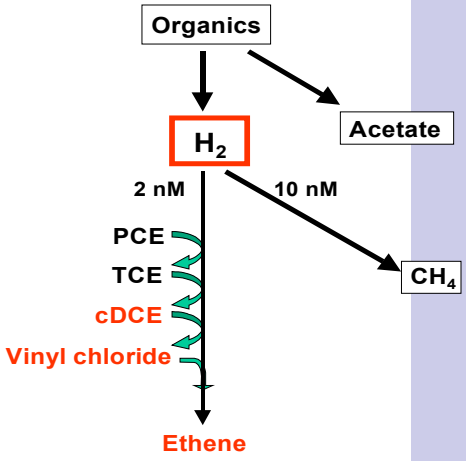
Collaboration Type: Mission directed *Fiscal Year:* 2000
Collaborator: (see description)
Collaborating Organization: (see description)

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

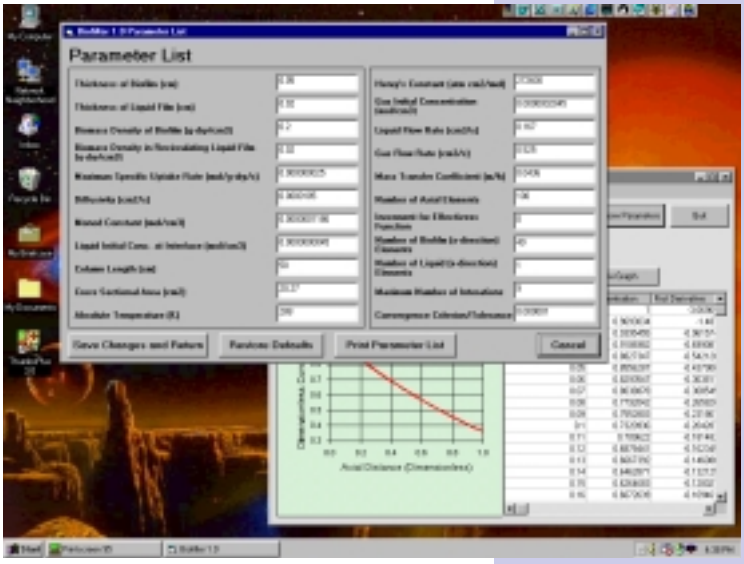
PI: Dr. Brian H. Davison *Institution:* ORNL

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

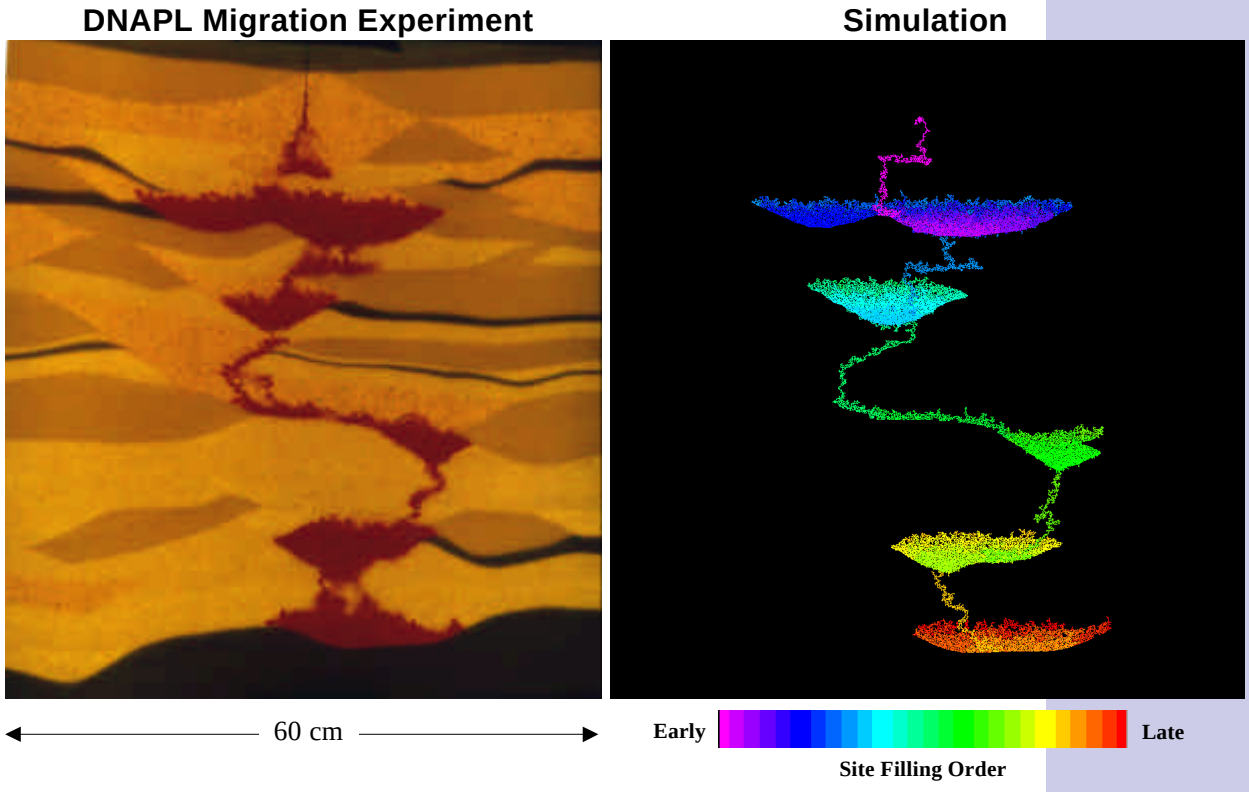
Description: Our work is similar to the work done for EMSP Project #70121, "Influence of Calcium Carbonate Grain Coating on Contaminant Reactivity in Vadose Zone Sediments" with different kinds of cores being examined. We are working to develop a technology/research transfer between the two projects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

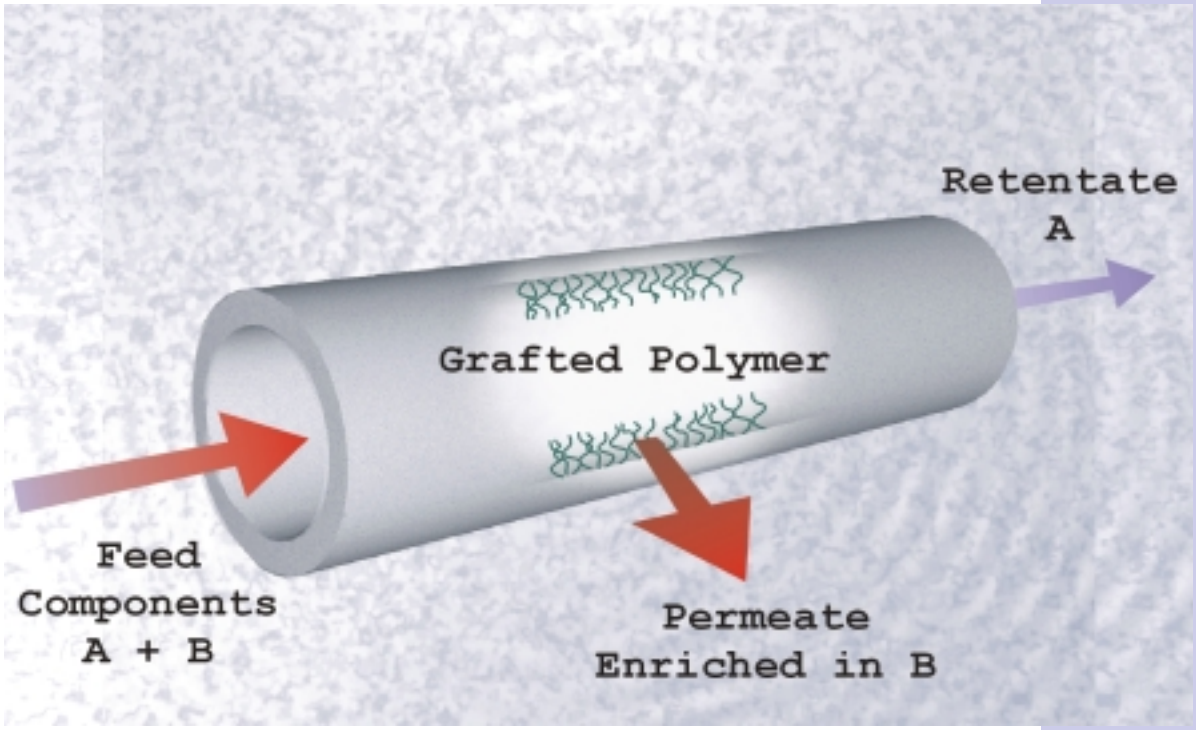
Separations Chemistry

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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