

INEEL/EXT-2000-01351

January 2001

Environmental Systems Research Candidates FY 2000 Annual Report

D. L. Miller, Program Manager

S. J. Piet, Deputy Program Manager

Environmental Systems Research Candidates FY 2000 Annual Report

**D. L. Miller, Program Manager
S. J. Piet, Deputy Program Manager**

Published January 2001

**Idaho National Engineering and Environmental Laboratory
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Office of Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727**

ABSTRACT

The Environmental Systems Research Candidates (ESRC) Program, which is scheduled to end September 2001, was established in April 2000 as part of the Environmental Systems Research and Analysis Program at the Idaho National Engineering and Environmental Laboratory (INEEL) to provide key science and technology to meet the clean-up mission of the U.S. Department of Energy Office of Environmental Management, and perform research and development that will help solve current legacy problems and enhance the INEEL's scientific and technical capability for solving longer-term challenges. This report documents the progress and accomplishments of the ESRC Program from April through September 2000. The ESRC Program consists of 24 tasks subdivided within four research areas:

- A. **Environmental Characterization Science and Technology.** This research explores new data acquisition, processing, and interpretation methods that support cleanup and long-term stewardship decisions.
- B. **Subsurface Understanding.** This research expands understanding of the biology, chemistry, physics, hydrology, and geology needed to improve models of contamination problems in the earth's subsurface.
- C. **Environmental Computational Modeling.** This research develops INEEL computing capability for modeling subsurface contaminants and contaminated facilities.
- D. **Environmental Systems Science and Technology.** This research explores novel processes to treat waste and decontaminate facilities.

Our accomplishments during FY 2000 include the following:

- We determined, through analysis of samples taken in and around the INEEL site, that mercury emissions from the INEEL calciner have not raised regional off-INEEL mercury contamination levels above normal background.
- We have initially demonstrated the use of x-ray fluorescence to image uranium and heavy metal concentrations in soil samples.
- We increased our understanding of the subsurface environment; applying mathematical complexity theory to the problem of transport of subsurface contaminants.
- We upgraded the INEEL's high-speed computer link to offsite supercomputers from T1 (1.5 MB/s) to DS3 (45 MB/s). Procurements have initiated a further upgrade to OC3 (155 MB/s) with additional onsite computational power that should put the INEEL on the Top 500 Supercomputing Sites list.
- We developed advanced decontamination, decommissioning, and dismantlement techniques, including the Decontamination, Decommissioning, and Remediation Optimal Planning System.

CONTENTS

Abstract	iii
Introduction	1
Background	1
Scope.....	1
Selection Process	3
Review Process	3
Program Highlights.....	4
Highlights of Individual Research Tasks.....	6
Research Description	6
Science and Technology for Environmental Characterization.....	9
Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship	11
Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-Term Stewardship Concerns and Development of Improved Modeling Methods.....	21
Ion Mobility Spectrometry for Environmental Monitoring and In Situ Measurement of Hazardous Organics.....	35
Molecular Engineering and Genomics for Development of Environmental Biosensors Using Robust Biocatalysts.....	49
Biologically Based Catalysts as Sensors to Detect Contaminants in Harsh Service Environments	53
Determining Soil Moisture Over Wide Areas for DOE Site Stewardship Hydrology.....	63
Advanced Robotic Technologies for Remote Environmental Surveillance and Stewardship	71
Isobaric Groundwater Well for Precise Water Level Measurement Relevant to Long-term Surveillance and Stewardship	83
Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes	87
Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface	99

Subsurface Understanding	103
Geological, Geophysical, and Hydrological Environs of the INEEL Site	105
Complex Systems Theory Applied to Subsurface Transport	113
Ecological Engineering of Rhizosphere Systems.....	121
Investigation of Factors Influencing Cesium Mobility and Uptake In Plant/Soil Systems	141
Long-term Biogeochemical Destruction and Control of Aquifer Contaminants Using Single-Well Push-Pull Tests	155
Unified Hydrogeophysical Parameter Estimation Approach to Subsurface Contaminant Transport—Subsurface Imaging Collaboration with the Center for Subsurface Sensing and Imaging Systems	159
Innovative Approaches to Characterize Vadose Zone Hydraulic Properties	163
Environmental Computational Modeling.....	175
Computing Framework for Environmental Cleanup, Restoration, and Long-term Stewardship.....	177
Environmental Systems Science and Technology.....	183
Decontamination, Decommissioning, and Remediation Optimal Planning System for the Advanced Decontamination and Decommissioning System	185
Waste Characterization and Sorting Station for the Advanced Decontamination and Decommissioning Systems.....	191
Robotic Waste Packaging System for the Advanced Decontamination and Decommissioning Systems	195
Environmental Separations and Barriers.....	199
Proton Conducting Ceramic Membrane Applied to Spent Nuclear Fuel Stewardship	211
Spectroscopic Investigations at Solid-Supercritical Fluid Interfaces in Support of Advanced Supercritical Separation Techniques.....	221
Appendix A—Publications and Presentations	
Appendix B—Comparison of ESRC Tasks with EM Site Technology Coordination Group Needs	
Appendix C—ESRC Portfolio Characterization	

Introduction

Welcome to the fiscal year (FY) 2000 annual report of the Idaho National Engineering and Environmental Laboratory's (INEEL's) Environmental Systems Research Candidates (ESRC) Program. The ESRC Program was started in April 2000 and is scheduled to end in September 2001. As designed, the research and development being performed by the ESRC Program is providing key science and technology to (a) meet the clean-up mission of the U.S. Department of Energy (DOE) Office of Environmental Management (EM), (b) help DOE clean up the cold-war legacy both at the INEEL and across the DOE Complex, and (c) enhance the INEEL's ability to solve longer-term challenges, like DOE's environmental stewardship of former defense sites.

Background

In March 2000, Congress approved DOE's request to use \$10.7M of EM program funds at the INEEL to develop: "...a suite of research areas comprising a new program of critical importance to the EM mission both at the INEEL and across the DOE complex. These environmentally applicable new research activities will address an agenda responsive to long-term stewardship with a special emphasis on subsurface science." In April 2000, the ESRC Program was established at the INEEL to meet this challenge and to develop novel processes or materials to treat, decontaminate, or store hazardous or radioactive waste.

Scope

The ESRC Program's science and engineering research is targeted at four major research areas critical to EM:

- Environmental Characterization Science and Technology
- Subsurface Understanding
- Environmental Computational Modeling
- Environmental Systems Science and Technology.

The relevance of each of these research areas to EM's mission is illustrated in Figure 1. The ESRC Program's technical staff has developed 24 tasks subdivided within these four research areas to develop each area in more detail in a way that is consistent with commitments to DOE and to Congress. The INEEL's approach is to focus the research on addressing important EM needs while enhancing their key "technical capabilities" in areas important to EM. Enhancing key technical capabilities includes building additional scientific and technical proficiency, strengthening the research staff, and enhancing the INEEL's relevant EM research infrastructure. The research tasks were started in April and May 2000. The four research areas are described below.

Environmental Characterization Science and Technology

This set of research tasks explores the potential offered by novel or improved ways to measure or gather information that is important to assessing environmental issues. These research tasks should help obtain the quality and type of data needed to make DOE's environmental decisions more scientifically defensible. The research should improve the efficiency of data acquisition, processing, interpretation, and

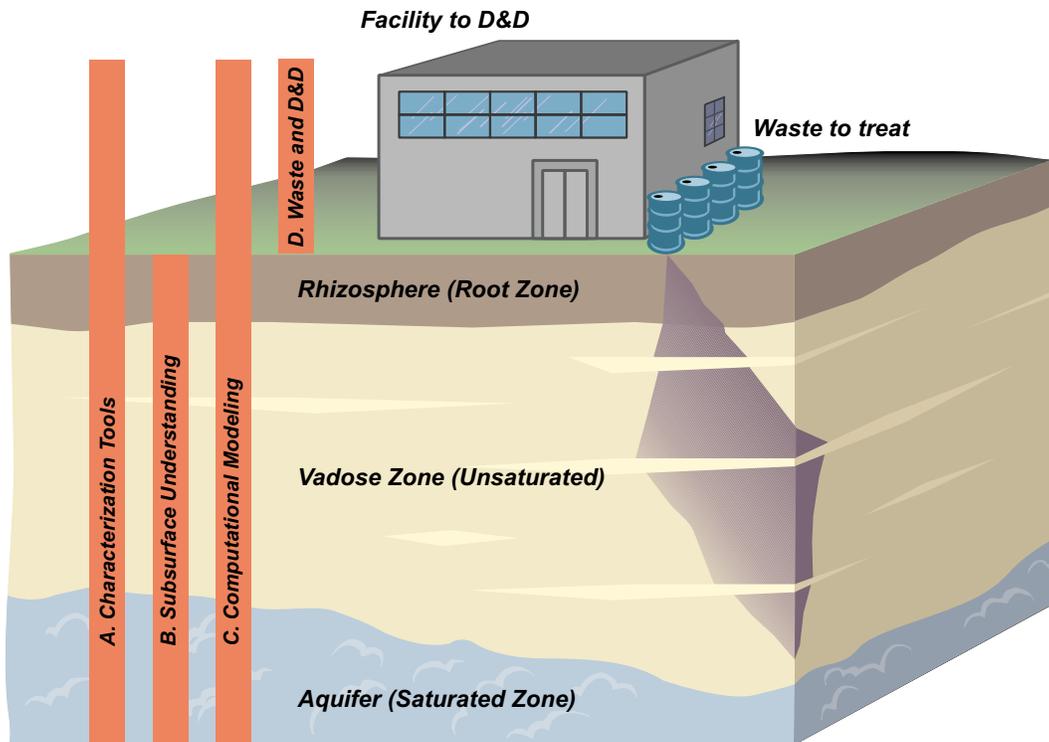


Figure 1. Relevance of research areas to EM’s mission.

use of environmental data. Most of the research tools being developed as part of this technical area should help us gather both more of and the right type of information required to understand the subsurface environment, which consists of the root zone, unsaturated (vadose) zone, and saturated groundwater (the aquifer). Some research tools developed will apply to assessing contamination above ground, either on the surface or in contaminated facilities. All of the research is relevant to broader issues of site characterization and monitoring for long-term stewardship of DOE facilities.

Subsurface Understanding

This research improves understanding of the complex subsurface environment and should advance the science to enable EM to model and manage waste and contamination problems more effectively. The research should enhance understanding of the biology, chemistry, physics, hydrology, and geology of types of waste and contaminants in the earth’s subsurface.

This research enhances our understanding of the complex interactions between contaminants and the environment at the range of physical scales (kilometers to microns) relevant to EM clean-up. Understanding how all aspects of the subsurface environment function and interact is critical to making good long-term remediation and disposition decisions.

Environmental Computational Modeling

This research develops computational science, modeling capabilities, and computing resources with an emphasis on current and future applications to EM. For example, technical tasks will be focused on modeling the behavior of chemical contaminants in the subsurface and modeling of contaminated facilities before decommissioning and decontamination. The goal of this research is to develop the

computing framework that can use the knowledge gained in research (such as that developed under the first two research areas) to more accurately model and predict what will happen to contaminants in the environment. This will allow DOE to make better and more informed decisions for clean up.

Environmental Systems Science and Technology

This research explores novel processes or materials to treat, decontaminate, or store hazardous or radioactive waste.

Selection Process

Research to be performed as part of the ESRC Program has been selected from two principal sources:

- *Research tasks with prior foundations in the INEEL's discretionary research programs.* These are primarily research tasks that have a basis in prior discretionary research at the INEEL. These tasks had already passed a rigorous technical peer review and were positively evaluated by the DOE Idaho Operations Office (DOE-ID) and by the INEEL EM Program staff who are cognizant of INEEL and DOE needs.
- *Invited new research tasks.* The INEEL's laboratory management solicited a small number of research proposals on critical additional subjects consistent with the four research areas; these are new research tasks relevant to subsurface science, environmental computational modeling, and long-term stewardship. INEEL experts familiar with EM needs and with INEEL research capabilities worked with the Lab's management to identify what technical areas should be targeted for invited research.

Review Process

All research proposed for this program passed the following four independent rigorous reviews to be started, and a fifth review to ensure that the work was on track after it started:

1. *EM relevance review to ensure significance to the DOE EM mission.* The INEEL staff, who work in INEEL EM programs and who understand the science and engineering needs of EM, evaluated each task for its potential to solve critical EM problems. The results of these reviews categorized most research tasks as both contributing to the understanding of the subsurface environment and important to long-term stewardship of DOE's contaminated sites—over \$7M of the \$10.7M was categorized as contributing to subsurface science and over \$8M of the \$10.7M was categorized as contributing to long-term stewardship. The rest of the research tasks advance knowledge in other environmental areas, such as waste management and decontamination of facilities.
2. *Technical review to ensure high technical quality.* The technical review ensured that only research of high technical potential was funded. The technical review provided constructive feedback to help principal investigators implement the research tasks that were ultimately funded.
3. *Management review to ensure adherence of each task to ESRC scope and purpose.* INEEL management reviewed all research tasks to make sure that the work was consistent with the ESRC objectives agreed upon with DOE and with the direction and intent of the Congressional reprogramming approval.

4. *DOE reviews.* In consultation with DOE-EM Science and Technology, DOE-ID reviewed the proposed research tasks and work packages and then approved the content prior to initiating work.
5. *Annual external peer and progress review.* All research performed in the Environmental Systems Research (ESR) Program, including these tasks in the ESRC Program, was reviewed in July 2000 by an external scientific and technical peer review committee. The peer review ensured that the work is meeting required scientific and technical standards and is progressing according to the research outline for the particular task. Twenty-one of 24 tasks were graded as meeting or exceeding expectations. The primary issue with the other three tasks was slow startup, given the history of the program; they are being helped and guided accordingly. The review also ensured that the work is appropriately targeted to solving real scientific and technical needs.

Program Highlights

Twenty-four research tasks were selected and approved. A 25th research task, “Advanced Environmental Geophysics and Geoscience Research,” will be started in FY 2001. The research has produced 20 papers and reviewed reports and 15 presentations (see Appendix A). As described below and in Appendix B, all ESRC tasks have been mapped to EM needs as listed in the INEEL Site Technology Coordinating Group (STCG) lists of needs and opportunities.

This year, through the coordinated efforts of the ESRC Program and research and development (R&D) integration, we established a systematic approach to ensure that EM research tasks are relevant to operational needs. This successful effort provided a methodology to facilitate and expedite the development and transition of science and technology to Site Operations. The real improvements in communications and potential beneficial impact on operational programs provide opportunities to significantly enhance EM performance, reduce costs, and efficiently manage our R&D effort.

A series of ESRC seminars has been established to inform the INEEL environmental management community of the progress and accomplishments of ESRC research.

We have categorized the ESRC research portfolio from the standpoint of the seven EM stages or “gates” of technology maturity:

1. Basic Research
2. Applied Research
3. Exploratory Development
4. Advanced Development
5. Engineering Development
6. Demonstration
7. Deployment.

As shown in Figure 2, two-thirds of the funded work is applied research; this is appropriate given ESRC objectives. Also consistent with the objectives and nature of ESRC, none of the tasks were categorized at Stages 5 through 7.

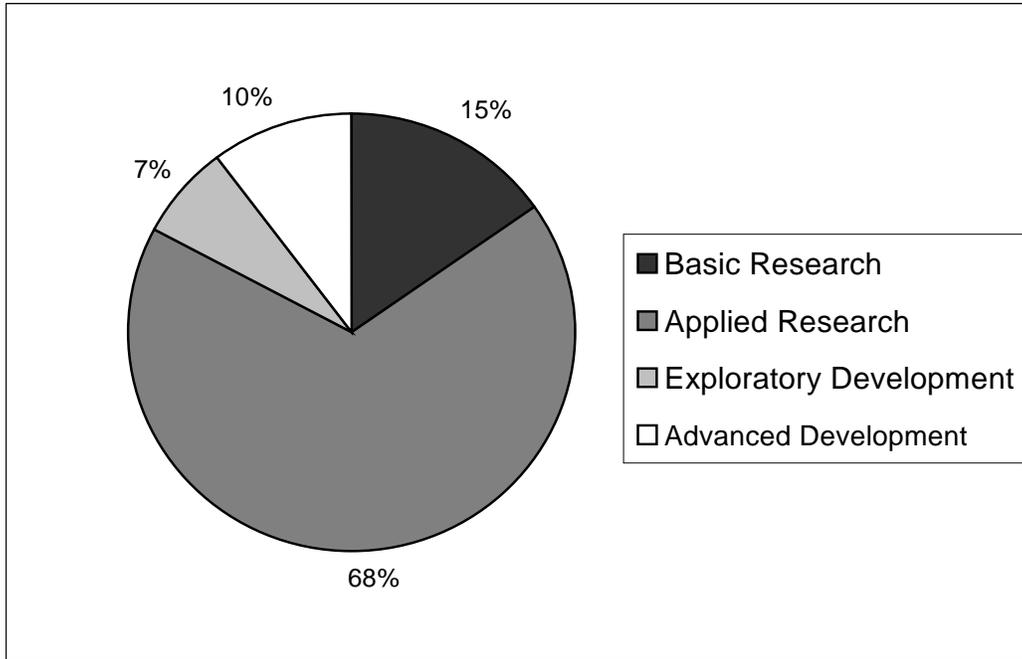


Figure 2. ESRC portfolio by technology maturity.

We have also categorized the ESRC portfolio from the perspective of the ESRC objective to enhance the INEEL’s science and technology capabilities for longer-term challenges, such as environmental stewardship. Appendix C provides additional explanation. Two-thirds of the nine INEEL R&D capability areas will be improved by ESRC research. The following disciplines are primarily supported:

- Applied Engineering
- Biotechnology
- Chemistry and Chemical Engineering
- Earth Science
- Information Management Technologies.

We find that two-thirds of the 49 INEEL R&D capabilities will be improved by ESRC research. Consistent with ESRC objectives, the following capabilities are primarily supported:

- Environmental monitoring
- Groundwater hydrology and hydrochemistry
- Vadose zone hydrology and soil physics
- Modeling, simulation, and information visualization
- Environmental engineering

- Engineered systems.

Highlights of Individual Research Tasks

The following bullets provide a sample of the research highlights of individual ESRC tasks:

- Advanced chemical, biological, nuclear, and hydraulic environmental characterization methods are being explored. In the task, “Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship,” an electron accelerator-based nondestructive assay (NDA) system, using x-ray fluorescence, detected uranium and transuranics in soil samples representative of the INEEL Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area. The initial tests demonstrated that the XRF techniques could detect uranium and heavy metal concentrations of less than 100 ppm and also image sources in a rotating sand column with a resolution of less than 3-linear mm. The final demonstration tests in FY 2001 will provide proof-of-concept for using the detection capability for characterizing materials in various soil environments. The data can be used in benchmarking subsurface science predictive models for many materials of interest.
- In the task, “Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-term Stewardship Concerns and Development of Improved Modeling Methods,” analysis of samples in and around the INEEL site show that mercury emissions from the INEEL calciner over the past 36 years have not raised regional off-INEEL mercury contamination levels above normal background.
- Improved understanding of the subsurface environment is being gained. For example, the task on, “Complex Systems Theory Applied to Subsurface Transport,” applies mathematical complexity theory to the problem of transport of subsurface contaminants.
- The INEEL’s high-speed computer link to offsite supercomputers for EM purposes has been upgraded by the task, “Computing Framework for Environmental Cleanup, Restoration, and Long-Term Stewardship,” from T1 (1.5 MB/s) to DS3 (45 MB/s). Procurements have initiated a further upgrade to OC3 (155 MB/s) with additional onsite computational power that should put the INEEL on the Top 500 Supercomputing Sites list.
- Advanced decontamination and dismantlement techniques are being developed, including the task, “Decontamination, Decommissioning, and Remediation of Optimal Planning System for the Advanced Decontamination and Decommissioning Process.

Research Description

The rest of this document describes the individual research tasks. These descriptions are grouped under the four research areas described above. Figure 3 shows the areas on the INEEL where research tasks are being conducted.

- ANL-W Argonne National Laboratory - West
- CFA Central Facilities Area
- INTEC Idaho Nuclear Technology and Engineering Center
- NRF Naval Reactors Facility
- PBF Power Burst Facilities
- RWMC Radioactive Waste Management Complex
- TAN Test Area North
- TRA Test Reactor Area
- WROC Waste Reduction Operations Complex

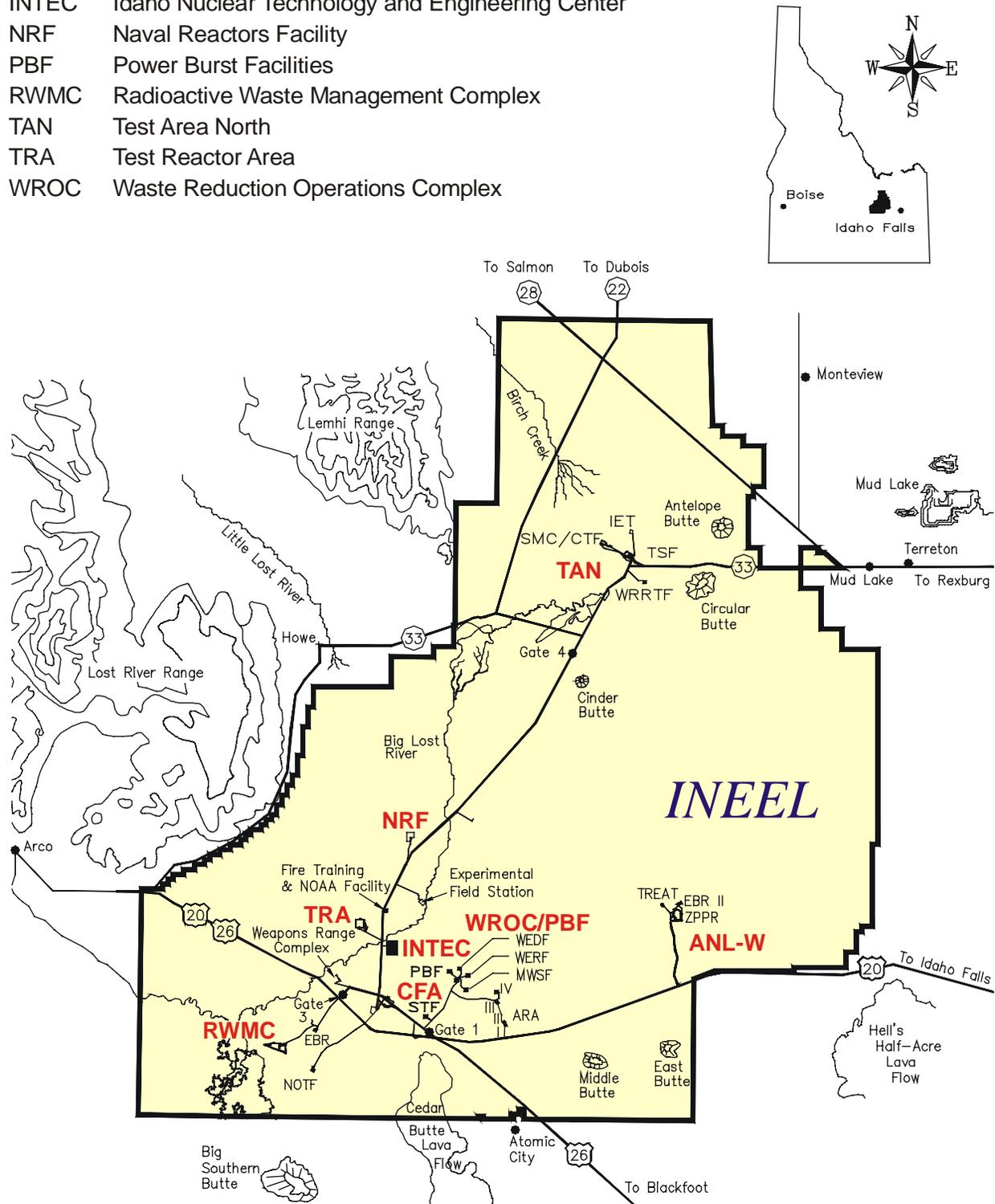


Figure 3. Map of the INEEL showing major facilities.

Science and Technology for Environmental Characterization

DOE needs sound scientific data so it can make sound decisions about our environment. This requires reliable chemical and biological data from air, water, and land. The research tasks in this section were chosen because they will provide the best possible science and technology available to characterize the environment. The research methods used in these tasks include mechanical, electrical, chemical, and microbiological techniques, and the use of robotics, modeling, enzymes, and other innovations.

Of special concern is the need to locate, identify, and quantify hazardous materials (certain organics, heavy metals, and radioactive isotopes) that have the potential to poison transient environments, such as the atmosphere or groundwater. A special emphasis in this work is the study of the subsurface, which has been inherently difficult to characterize. In all aspects of this work, the goal is to improve the acquisition, processing, interpretation, and use of environmental data.

The following tasks are reported in this section:

- Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship
- Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-Term Stewardship Concerns and Development of Improved Modeling Methods
- Ion Mobility Spectroscopy for Environmental Monitoring and In Situ Measurement of Hazardous Organics
- Molecular Engineering and Genomics for Development of Environmental Biosensors Using Robust Biocatalysts
- Biologically Based Catalysts as Sensors to Detect Contaminants in Harsh Service Environments
- Determining Soil Moisture Over Wide Areas for DOE Site Stewardship Hydrology
- Advanced Robotic Technologies for Remote Environmental Surveillance and Stewardship
- Isobaric Groundwater Well for Precise Water Level Measurement Relevant to Long-Term Surveillance and Stewardship
- Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes
- Using Environmental Records in Mid-Latitude Glacier Ice to Better Define Environmental Management Contaminant Inputs to the Subsurface

Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship

Looking at Subsurface Samples with Nondestructive Techniques

Michael J. Connolly, Gail Cordes, James L. Jones, John C. Determan, Greg K. Becker

SUMMARY

A critical part of any environmental remediation effort is a scientifically based assessment of the hazards at the site, and the risks involved with the cleanup activities. There is a constant need to be able to quantitatively characterize materials without disturbing or degrading them. This is especially true of waste and radioactive materials, such as waste containers, but also true of subsurface samples or in-field measurements.

This task collectively supports environmental stewardship and long-term monitoring by (a) providing intelligent information processing techniques for the interpretation and review of nondestructive assay (NDA) measurement data, (b) demonstrating proof-of-concept for using a novel accelerator based NDA technique in support of subsurface science predictive model development, and (c) validating and verifying NDA system operation; work will continue into FY 2001.

Nuclear based nondestructive techniques enable materials assay without disturbing or degrading the materials, and typically prove to be faster, more environmentally benign, and cheaper than destructive analysis methods. Intelligent information processing techniques contribute to the speed and accuracy of data acquisition. Such techniques can provide rapid to real-time data validation, verification, analysis, and interpretation of the measurement data as well as the NDA system operation. This task involves three specific subtasks:

1. Evaluating intelligent information processing methods for application to NDA techniques, including accelerator-based methods. Neural networks approaches will be used on measurement data sets from two neutron waste assay measurement systems. During FY 2000, the Advanced Data Validation and Verification System, a multivariate analysis software package, was modified to monitor operation of the accelerator-based NDA system in Subtask 2, the software was trained with a subset of the accelerator operational data, and the system was successfully demonstrated in preliminary tests.
2. Assembly and demonstration of an accelerator-based NDA system on a laboratory simulation of subsurface isotope movement. The NDA system is located at the Idaho Accelerator Center (IAC) of the Idaho State University (ISU) and uses x-ray fluorescence (XRF) and nuclear resonance fluorescence scattering to detect uranium and transuranics in soil samples representative of the Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area (SDA). During FY 2000, preliminary tests successfully demonstrated XRF techniques to detect uranium and heavy metal concentrations of less than 100 ppm and to image sources with a resolution of less than 3 linear mm.
3. Expansion of an existing expert system to allow easy modification of existing rules sets for application to different waste forms and demonstrate this new capability by adapting existing rule sets for application to debris type waste forms. The measurement data are passive/active

neutron data and gamma ray spectroscopy data, from waste drum assay systems at the INEEL's Stored Waste Examination Pilot Plant (SWEPP). The data are reviewed with the expert system to verify that measurements are self-consistent and reasonable and that there are no biases in the data that are unaccounted for. During FY 2000, the debris rule requirements were specified and the new rule editor system was designed.

TASK DESCRIPTION

This task collectively supports environmental stewardship and long-term monitoring by (a) providing intelligent information processing techniques for the validation and verification of NDA system operation, (b) demonstrating proof-of-concept for using a novel accelerator based nondestructive assay (NDA) technique in support of subsurface science predictive model development, and (c) interpretation and review of NDA measurement data.

This task involves three specific subtasks:

1. Evaluation of intelligent information processing methods for application to NDA techniques, including accelerator-based methods.
2. Assembly and demonstration of an accelerator-based NDA system on a laboratory simulation of subsurface isotope movement.
3. Expansion of an existing expert system to allow easy modification of existing rules sets for application to different waste forms and demonstrate this new capability by adapting existing rule sets for application to debris type waste forms.

Intelligent Information Processing Techniques (Subtask 1)

This subtask applies pattern recognition techniques to nondestructive assay (NDA) processes to assist and improve NDA system design; provide measurement data acquisition strategies, data reduction methods, and data interpretation; and provide hardware operation status and data validation.

Pattern Recognition for NDA Measurement Data Sets

This task evaluates state of the art NDA measurement processes to exploit acquired data sets for information not noted or used in conventional data analysis techniques. Neural network approaches will be used to identify and extract unknown data features and relationships not used due to constraints inherent in conventional approaches. Features and relationships of interest are those which can be used to improve NDA system design, data acquisition strategies, data reduction methods, and data interpretation. Conventional approaches to these NDA process categories are generally based on first principle techniques which, for the most part, are time and resource intensive and in many cases subject to unknown error components. Often conventional techniques are incapable of recognizing the presence of a bias source and therefore it is not corrected for in the NDA assay quantification.

The purpose of this task is to address certain nondestructive assay measurement deficiencies. The neural network pattern recognition techniques are being applied with the intent of demonstrating benefit through either reduction in required resources or gain of information in the overall NDA process. These techniques have a potential to yield benefit in quantifying the following three known biases in NDA systems: radioactive material spatial dependent bias; radioactive material physical form dependent bias; and matrix elemental composition, density, and spatial distribution.

These known deficiencies are to be processed relative to the ability of neural network techniques to properly identify presence or absence in complex NDA data patterns. The following general steps are used in this task to guide the evaluation of neural networks to NDA processes:

1. Evaluate at least three existing neural network pattern recognition techniques for suitability and subsequent application to NDA data sets.
2. Use actual data sets that are known in terms of the measurement configuration, namely, selected data from the Los Alamos National Laboratory (LANL) Crated Waste Assay Monitor (CWAM) and NIS-6 Combined Thermal Epithermal Neutron (CTEN) assay systems, and apply the neural network pattern recognition techniques to the data.
3. Identify instrument response data patterns attributable to specified bias sources (listed above) contained in the selected data sets.
4. Define capabilities and limits of selected neural network pattern recognition techniques to detect the presence of selected bias sources through data features and relationships, and other information related to the measurement.
5. Evaluate the useful features identified in Step 4 per their physical meaning and in what manner they can be used in NDA measurement improvement.

During FY 2000, NDA measurement system data sets were selected for use in this task. These data sets were recorded from the LANL CWAM and NIS-6 CTEN assay systems. Both of these systems are neutron measurement systems. The data sets are comprised of many different measurement sample configurations, each with known source/matrix configurations. Each measurement consists of hundreds of data fields. Arrangements were made to acquire and understand the acquisition and reduction parameters of the data sets.

In FY 2001, the various data sets will be formatted and cataloged as to inherent characteristics that will be useful in later intelligent processing manipulations. Some additional data sets from LANL will be added to the files already in place. Investigation into appropriate neural network pattern recognition techniques and hybrids will continue.

Pattern Recognition for NDA System Operability Data Sets

The purpose of this task is to provide a proof-of-principle for the use of pattern recognition intelligent information processing methods to improve the speed and quality of NDA techniques. Pattern recognition techniques provide real-time capability to monitor the performance of NDA hardware systems and interpret the resulting performance data by acting across the time stamped vector of system parameters. One of the pattern recognition techniques available at the INEEL, the Advanced Data Validation and Verification System (ADVVS), has been selected for this task. The software will be demonstrated on the Varitron accelerator and detectors in the hardware system being built at the IAC at ISU for Subtask 2. The ADVVS algorithms are proprietary to Dr. Jack Mott of Advanced Profiling Inc., in Idaho Falls. The INEEL and Dr. Mott have entered into a nondisclosure agreement and the INEEL is using his expertise and our existing software license in this task under a services subcontract.

The ADVVS is a pattern recognition technique using multivariate analysis of incoming data. The real-time data values are compared with data estimates calculated from functional relationships that model known modes of system operation or system data outputs. Any statistically significant deviation from these calculated patterns is flagged. Depending on the specific application, the system operation may

be modified or terminated. The data deviations may be analyzed offline and a new data included in the functional relationships if it is adopted and classified as normal but unanticipated. In the future, this same approach potentially could be used on the output measurement data to recognize and categorize the results of the nondestructive interrogation. Thus, the entire variable vector is considered a pattern and is analyzed in real time to recognize pattern changes that can be interpreted as data characteristics or operating system anomalies.

During FY 2000, the ADVVS was installed on a Windows NT machine at the INEEL and rerun to ensure that the software would now run and give proper results in a DOS window in the Windows NT environment. This version of the software was originally used in the early 1990s during the electric vehicle (EV) battery tests and vehicle field tests.

The LabView-ADVVS interface was developed, and ADVVS was updated for the subsurface science research.

Seven of the 22 data signals from the Varitron were logged and the data files were analyzed using ADVVS. These preliminary results show that additional sensors initially thought to be unnecessary for the analysis actually could contain important information that would contribute to accurate analysis of the accelerator beam current. It was also shown that some sensors were malfunctioning and require calibration; some data spikes represent anomalous system noise that can be filtered prior to analysis; and the source of a periodicity in the beam current data was identified as the wave-guide tube cooling system that is manually operated (chilled water is injected into a cooling jacket around the wave-guide tube when the temperature reaches a predetermined set point, roughly every 2 or 3 minutes). The LabView, ADVVS, and Varitron-Operator interfaces were programmed, tested, installed on the IAC Varitron accelerator control computer, and field-tested with the seven data signals. The capability to handle all 22 available signals was included in the programming.

The preliminary results using seven signals indicated that running the Varitron accelerator is currently an art form that has few precisely repeatable operating procedures. To allow a better analysis of the operational data, a test matrix has been proposed to provide the necessary reference data to estimate a beam current and energy for any setup that is within the established operating range. During FY 2001, the expanded set of operational data will be logged using a test matrix of both short and long pulses for a range of electron beam energies between 4.5 and 13.5 MeV. The ADVVS will be trained against the expanded set of data. Signals from the detectors will be added and the software will be run real-time with the Varitron on a stand-alone basis and then with the integrated system assembled for the subsurface science research work of Subtask 2.

With the completion of this subtask, the proof-of-concept will be demonstrated for using the ADVVS software for monitoring the operability of accelerator-based systems in subsurface science research and applications.

Accelerator Based NDA Technique in Support of Subsurface Science Predictive Model Development (Subtask 2)

This subtask demonstrates the proof-of-concept of applying an electron accelerator-based system to the detection of uranium, transuranics, and heavy metals in soil samples representative of the Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area (SDA). This subtask leverages heavily on the “unconventional” XRF and nuclear resonance fluorescence (NRF) scattering research being developed and tested at the IAC and supported by the FY 2000 INEEL/ISU Accelerator Alliance Initiative. Initial “unconventional” XRF results at the IAC, before Subtask 2 began, allowed thorium characterization through about 1 cm of lead shielding.

In this interrogation process, an accelerator accelerates electrons up to several MeVs in kinetic energy. These electrons interact with a high-Z material to produce high-energy bremsstrahlung (photons). Based on the selected electron beam energy, these photons are highly penetrating. These penetrating photons will probe atomic energy levels (up to 100s keV) in the XRF process during the accelerator pulse, and will probe nuclear scattering/excitation levels (up to 10 MeV) in the NRF process after the accelerator pulse. The unconventional nature of the NRF and XRF comes from the use of these high-energy, highly-penetrating bremsstrahlung photons, the high-intensity level of XRF/NRF stimulation, and the associated specialized detection systems.

Specifically, this demonstration involves identifying and characterizing inhomogeneous uranium, americium, and neptunium materials in several applicable soil samples. Initially, a 6-MeV electron accelerator will be used as the investigating probe and up to three detectors: a thin window (~1%) high-purity germanium, a larger volume (~10%) high-purity germanium, and a large 5 × 5 sodium iodide (NaI). The variable-energy Varitron electron accelerator will additionally be included in the research. For each soil sample, the detection limit of each nuclear material will be defined as a function of soil thickness and nuclear material quantity. If time and costs permit, combinations of these inhomogeneous samples can be investigated as well as effects from using homogenous distributions and higher electron beam energies.

During FY 2000, the experimental test stand was designed and constructed and initial tests were run with the 6-MeV accelerator. The testing configuration consists of an electron accelerator in one room and the soil-sample stand in an adjacent room. The accelerator is a 6 MeV, S-band-type, electron accelerator oriented to direct energetic (up to 6 MeV) photons into a collimator assembly consisting of a 20.3-cm hole in a 3-m thick concrete facility wall. Each end of the hole is supplied with custom-built, stainless-steel end plugs containing a 1-cm-diameter hole. The soil sample stand consists of a vertically oriented, 1-m-tall, up to 25-cm-inside-diameter Plexiglas tube atop a rotating stand assembly. Initial tests are using a 60% high-purity germanium and two beryllium-windowed, low-energy sensitive germanium detectors to measure the induced annihilation and XRF radiation emissions.

The test plan includes the initial use of standard clean sand with uniform density and good compaction properties. These initial tests will include saturated and unsaturated characterization assessments of additive sample types and quantities for both imaging and elemental analysis, including uranium, chromium, and cadmium. Other sample and soil types will be determined based on the initial results.

A photo of the experimental test configuration is shown in Figure 1. Its associated process schematic is shown in Figure 2. The testing configuration consists of an electron accelerator in one room and the soil sample stand in an adjacent room. The accelerator is a small 6 MeV S-band-type electron accelerator (see Figure 3) oriented to direct energetic (up to 6 MeV) photons into a collimator assembly consisting of a 20.3-cm hole in a 2-m-thick concrete facility wall.

Preliminary FY 2000 tests using sand in the soil column have been very successful using XRF techniques. The tests showed that it is possible to detect uranium and heavy metal (high Z down to ~30 Z) in the soil column at concentrations below 100 ppm. Lower concentration levels can be detected for materials with higher Z. Three-D images were formed of the rotating soil column to determine spatial resolution of the XRF technique, and it was found that the linear resolution was less than 3 mm. Work will continue into FY 2001.



Figure 1. Subsurface science research test configuration showing vertical soil column and detectors.

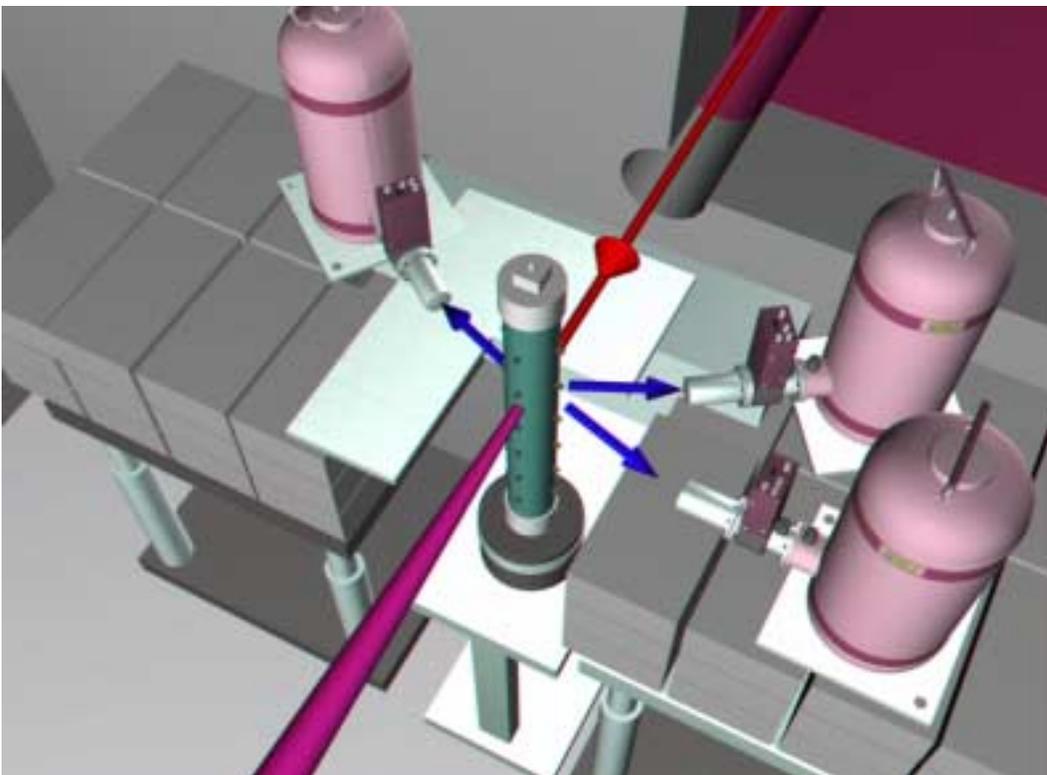


Figure 2. Test configuration schematic.

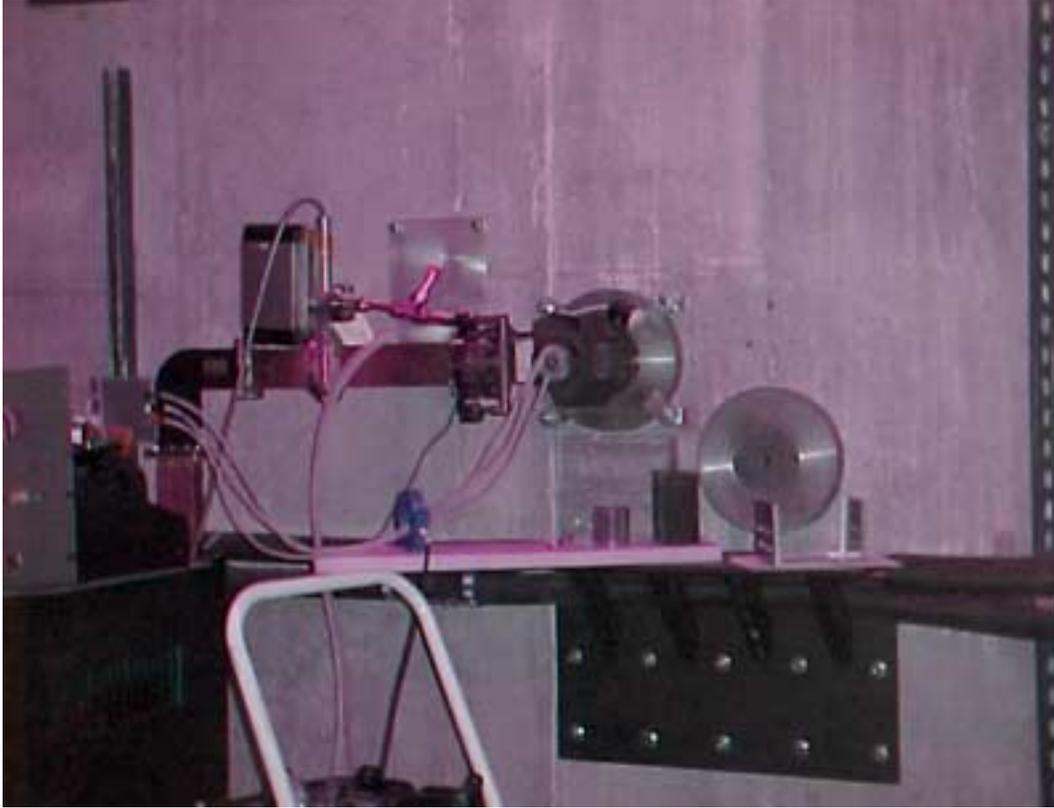


Figure 3. The 6 MeV accelerator positioned in room adjoining the test configuration.

The results of the Subtask 2 demonstration tests will provide proof-of-concept for using this the detection capability for characterizing these nuclear materials in various different soil environments (homogenous dispersal, wetness factor, soil grain surface effects, microorganism effects, mineral content, etc). This type of detection capability can be used very effectively in the future in helping benchmark numerous subsurface science predictive models for many materials of interest.

Modify and Demonstrate INEEL CLIPS Based NDA Expert System for Application to Transuranic Debris Waste Forms (Subtask 3)

Subtask 3 will modify the NDA Data Review Expert System (NDA-DRXS), an INEEL CLIPS-based NDA expert system for transuranic sludge waste, and provide proof-of-concept for using the modified system for other waste forms by demonstrating the modified system on transuranic debris waste forms. The expert system is being developed to review transuranic waste nondestructive assay data. The measurement data are passive/active neutron data and gamma ray spectroscopy data, both off of waste drums at the SWEPP. The review is performed to verify that measurements are self-consistent and reasonable, and that there are no biases present that have not been accounted for.

The current design of NDA-DRXS allows for easy adaptation of the generic framework to different waste assay configurations through an innovative combination of rule-based and object-oriented programming techniques. The initial set of validation rules dealt explicitly with sludge waste forms. But many of these rules can be modified to be applicable to other waste forms. The ability to make the system easily adaptable to different waste forms, such as debris waste forms, had not been developed prior to FY 2000, but is of importance to both our internal and external customers. Improving system adaptability also

addresses the important issue of expert system maintenance. Customers need to know that as their domain experience grows, the capabilities of the expert system will also be able to progress. Rule update and maintenance should not require a software specialist, but should be performable by knowledgeable users of the expert system.

The key issue here is to address the form of knowledge representation in a systematic manner. Therefore, this work will include the following steps:

1. Discover the structure, or “grammar” of data validation rules. Rules are currently available for two different organizations, already specified in the CLIPS expert system language. These rules would provide the raw material for determining the structure, or common form and necessary elements, of validation rules.
2. Design a validation rule representation that is consistent with the analysis in Step 1.
3. Specify one of the sets of validation rules in the new format.
4. Design a user interface based on this format for performing validation rule updates, modification, and maintenance. The interface would require specific inputs from the user and would update the validation rules; therefore, specific knowledge of the Clips expert system language would not be required for modification and update of validation rules.
5. Use the interface to adapt the sludge validation rules to be appropriate for another waste form, such as debris, as a demonstration of the capability.

Discovering the structure of validation rules will benefit future work that has been proposed for FY 2001. The proposed work is more ambitious than the system for rule maintenance/editing that is being developed under Subtask 3. It is a system for rule specification that could be used by a nonsoftware specialist, in particular, a domain expert. With the structure of validation rules already known, a simple language for rule specification could be designed, or perhaps adapted from an existing specialized computer-based language. A language translator could then be designed, or adapted. Finally a tool for rule specification would be built that would accept user input describing a validation rule, and then use the translator to produce validation rules in the CLIPS expert system language.

The completed system will improve the throughput of waste containers at SWEPP and the consistency and quality of the data review process.

ACCOMPLISHMENTS

This section summarizes accomplishments for FY 2000 for the three subtasks. The work will continue into FY 2001.

Subtask 1

Most of the files of waste, assay data sets were cataloged for the neural network research.

The ADVVS software was updated for the subsurface science research. The LabView, ADVVS, and Varitron-Operator interfaces were programmed, tested, installed on the IAC Varitron accelerator control computer, and field-tested with seven of the 22 Varitron data signals. The preliminary tests showed that the ADVVS can be used to monitor the operation of an accelerator like the Varitron and reveal important operational information. For example, it was shown that some sensors were malfunc-

tioning and that some data spikes represent anomalous system noise that should be filtered. The tests identified the source of a periodicity in the beam current data. The tests further showed that the remaining 15 sensors initially thought to be unnecessary for the analysis actually could contain important information that will contribute to accurate analysis of the accelerator beam current.

Subtask 2

Preliminary subsurface science research tests during FY 2000 using sand in the soil column were very successful. The tests used XRF techniques and showed that it is possible to detect uranium and heavy metals (high Z down to $Z \sim 30$) in the soil column at concentrations below 100 ppm. Lower concentration levels can be detected for materials with higher Z. Three-D images were formed of the rotating soil column to determine spatial resolution of solid sources using the XRF technique, and it was found that the linear resolution was less than 3 mm. Recently, ISU and Boise State University have obtained 3-year funding of \$180K for follow-on work to this subtask. The funding comes through the Inland Northwest Research Alliance of the INEEL.

Subtask 3

The debris rule requirements were specified and the debris rules were manually produced, thus greatly extending the applicability of the NDA-DRXS with respect to the types of waste streams encountered at the SWEPP facility. The rule editor system was designed with three components: a database to store the data needed to form CLIPS code, a program to form CLIPS code from the database, and a program to allow editing of the database entries. The database was designed to store not only data needed to build CLIPS code, but enough information to build the C++ code used to initialize key CLIPS structures from the waste measurement database. An initial design for the CLIPS code building program was produced as an object model. A rule editor to operate on the rule structure database was partially designed (an object model). The rule editing tool when complete will make the expert system more flexible, and also speed the process of specifying new expert system rule modules.

REFERENCES

None

Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-Term Stewardship Concerns and Development of Improved Modeling Methods

Understanding the Movement of Mercury in the Environment Surrounding the INEEL

Michael L. Abbott

SUMMARY

Environmental fate and transport of the toxic air pollutant mercury (Hg) is currently a high-priority regional concern for the INEEL, and national and global concern for the U.S. Environmental Protection Agency (EPA). At the INEEL's Idaho Nuclear Technology and Engineering Center (INTEC), significant quantities (est. 40 kg/year) of Hg may have been released over 37 years of Environmental Management's (EM's) high-level waste (HLW) calcination operations. The EPA is very concerned about the continued global buildup of Hg in the atmosphere and aquatic ecosystems, and has recently invested heavily in Hg research to better understand its complex environmental cycling.^{1,2} This task is a joint INEEL and U.S. Geological Survey field research effort to better understand the fate of Hg emissions (operational component) from the INEEL's calciner (New Waste Calcining Facility [NWCF]) and contribute at a national level to the scientific understanding of local, regional, and global Hg fate and transport (research component). This task consists largely of Hg fallout sampling in precipitation and soils in two geographic areas: the INEEL and surrounding airshed, which includes the Eastern Snake River Plain and adjacent elevated areas; and two high-elevation, mid-latitude glaciers—the Upper Fremont Glacier (UFG) in Wyoming and the Inilchek Glacier in Central Asia. Glacial snowpack provides a preserved annual record of both regional and global Hg fallout that can be used to answer questions about long-range INEEL transport and help to fill existing data gaps on the relative importance of local versus global source contributions to fallout.

Samples of snow ($n = 130$), rain ($n = 6$), soil ($n = 103$), and air ($n = 5$) were successfully collected on the INEEL and at 11 regional background sites from January through March. Analytical results for snow before startup of the calciner indicated relatively low Hg concentrations within the range of the western regional background (3 ng/L) and unexpectedly high concentrations (10 to 20 ng/L) near INTEC, which may be due to Hg evasion from the soil followed by entrapment in the overlying snowpack. Because startup of the NWCF was delayed until March 15, 2000, and no appreciable snow fell after this date, snow sampling to determine NWCF fallout rates on the INEEL was not possible. Snow samples were successfully obtained from the UFG in May ($n = 20$) and the Inilchek in July ($n = 50$). The UFG data indicated very low (0.3 to 0.9 ng/L) concentrations relative to regional background, and the Inilchek samples have not yet been analyzed. Surface soil sampling around INTEC showed (a) very low Hg concentrations overall compared to background levels in similar soils across the U.S., (b) a 4% per cm reduction in Hg concentration with depth, and (c) significantly higher Hg concentrations in soils under shrubs (likely due to fixation by organic matter) and in depressions (likely due to Hg runoff). Using these data, mass balance calculations were able to account for approximately 40–300 kg of calciner Hg in the soil, which is only 3–20% of the estimated total Hg emitted over the 37-year calciner operating history. These results provide evidence that much of the Hg deposited from calciner operations may have been reduced in the soil and reemitted as Hg(0) to the global atmospheric pool.

TASK DESCRIPTION

Summary of Sampling Activities

Table 1 summarizes the multimedia sampling activities during FY 2000. All samples were analyzed for total mercury (THg), and a small fraction were analyzed for methylmercury (MHg). Total Hg includes all chemical forms of Hg, including (a) divalent Hg(II), which readily deposits and is the predominant form of Hg emitted by the calciner; (b) elemental Hg(0), which comprises the bulk of the global atmospheric pool, but does not readily deposit (until some of it is oxidized by downwind atmospheric chemistry); and (c) methyl mercury, which is of concern because it is a more toxic species and bioaccumulates in aquatic organisms (up to 10^7 times the water concentration). Snow and rain were sampled because these are the dominant scavenging mechanisms that transport Hg from the atmosphere to the ground, where it is of primary concern (see Reference 1). Also, precipitation concentrations can be linked with precipitation time intervals to calculate Hg deposition rates, which can then be used to validate deposition models. Snow was the primary sampling medium because it is the dominant form of precipitation in this region and because it usually remains on the ground, allowing sampling at a later date. However, because startup of the NWCF was delayed until March 15, 2000, and very little snow fell on the INEEL after this date, only five snow samples on the INEEL were obtained during NWCF operations. Because of the lack of the INEEL NWCF data, proposed source apportionment methods (principal component analysis and isotopic ratios) were not implemented. Limited rain sampling was done after this time because of the continuing dry conditions this spring and the difficulty of coordinating rain sampler deployment during the few short-term rainfall events that occurred. Soil sampling was successfully

Table 1. Summary of mercury sampling activities for FY 2000.

Location	Month/00	No. Samples	Analyzed?	Purpose
<u>Snow</u>				
INTEC 5-km Grid (Figure 1)	Jan 4–6	50	Yes	Pre-NWCF startup baseline
	Mar 17	8	Yes	Post-NWCF impacts
Background sites (10) (Figure 2)	Dec 20	15	Yes	Regional background surrounding INEEL
	Jan 17–19	24	Yes	
	Mar 25–26	34	Yes	
W. Slope Teton Range (5 sites from 6,000 to 10,000 ft)	Jan 17–18	20	Yes	1) High precipitation/fallout rates 2) Sensitive “downwind” ecosystem
Upper Fremont Glacier, WY (13,200 ft)	May 1–8	20	Yes	1) Long-range INEEL transport 2) preserved annual fallout record in snowpack
Inilchek Glacier, Asia (16,000 ft)	July	50	No	Global fate/transport data gaps
<u>Rain</u>				
INTEC Grid – NE1, NE2, NW1	May	6	Yes	1) Rain sampling method 2) NWCF fallout
<u>Air</u>				
INTEC Grid—1–4 km downwind of NWCF plume; rest area	Mar	5	Yes	1) Air sampling method, 2) regional background
<u>Soil</u>				
Experiment 1	Jul	24	Yes	Sampling methods-depth
Experiment 2	Jul	20	Yes	Sampling methods-vegetation
INTEC Grid	Aug	59	No	Residual cumulative deposition

accomplished in late summer to determine the Hg variability in soil (Experiments 1 and 2) and to estimate the cumulative residual Hg load in the soil around INTEC after 36 years of calcining operations.

Most of the sampling on the INEEL was conducted on the INTEC 5-km grid—an array of 64 sampling locations located on 22.5-degree radials at distances of 1, 2, 3, and 5 km (Figure 1). This grid was designed, based on previous air modeling studies of the INTEC 250-ft main stack,³ to provide an adequate assessment of the fallout pattern around the facility with a reasonable number of samples. The 10 background sites (Figure 2) were selected based on their location surrounding the INEEL, their likelihood of snowfall accumulation, and winter access. Snow was also sampled in January on an elevation gradient extending from the Teton Valley outside Driggs, Idaho (6,000 ft) to the summit of Grand Targhee Ski Area (10,000 ft). This area was selected because it (a) receives very high snowfall (maximizes air pollutant scavenging) and snow accumulation (allows sampling of a long-term fallout period), (b) is an optimum location to investigate changes in Hg fallout with elevation (current high interest to EPA), and (c) is located between the INEEL and concerned public interest groups in Jackson, Wyoming (stakeholder considerations). Snow sampling was conducted at the Upper Fremont Glacier (UFG) and Inilchek Glacier sites because of (a) the comprehensive annual fallout record preserved in their winter snowpack, (b) their mid-latitude locations and elevations, and (c) ongoing research activities at these locations by the U.S. Geological Survey, which allowed sharing of field trip expenses. The UFG site was also investigated to determine if long-range transport of Hg from the INEEL could be detected.

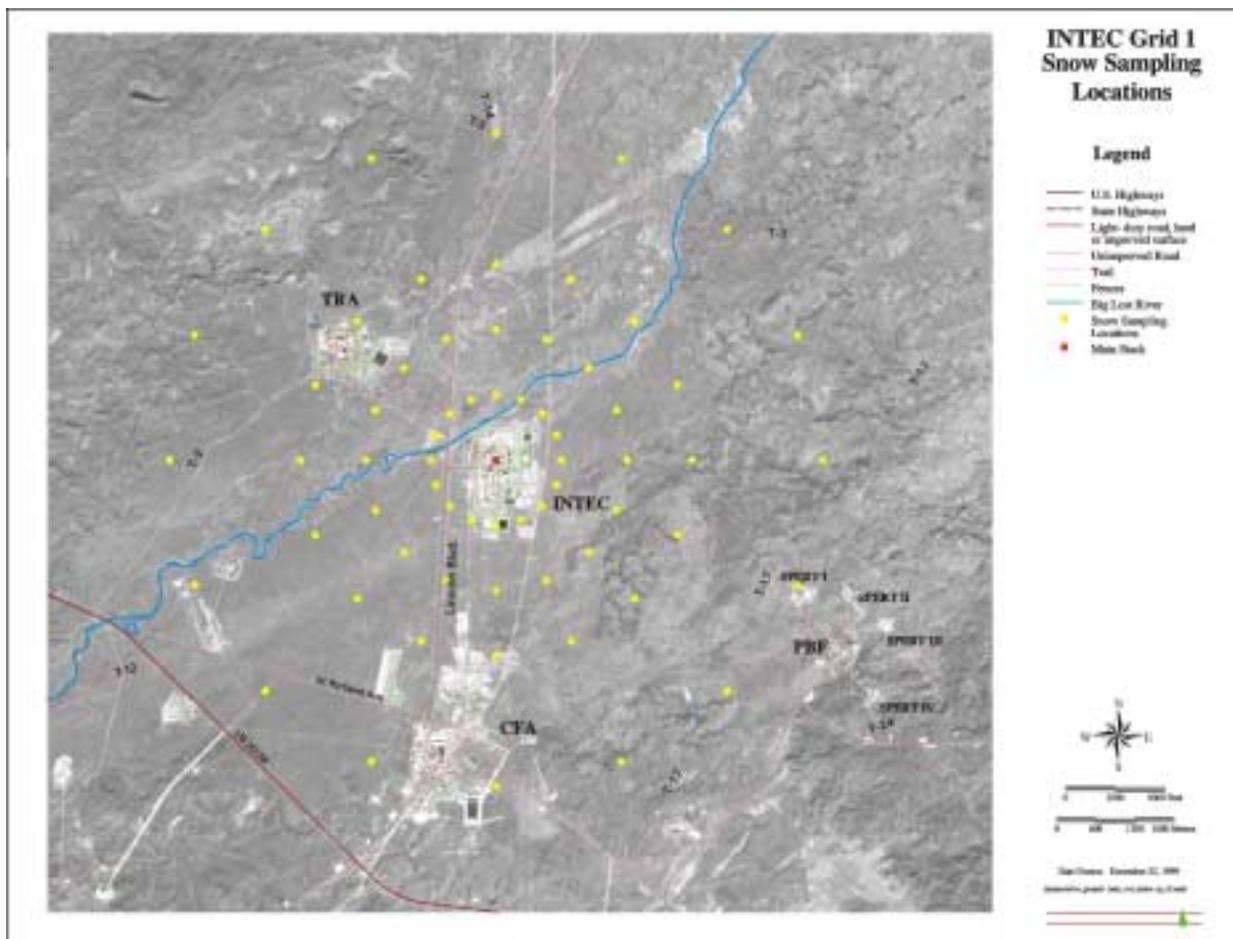


Figure 1. INTEC 5-km sampling grid—64 locations on 22.5° radials at distances of 1, 2, 3, and 5 km.

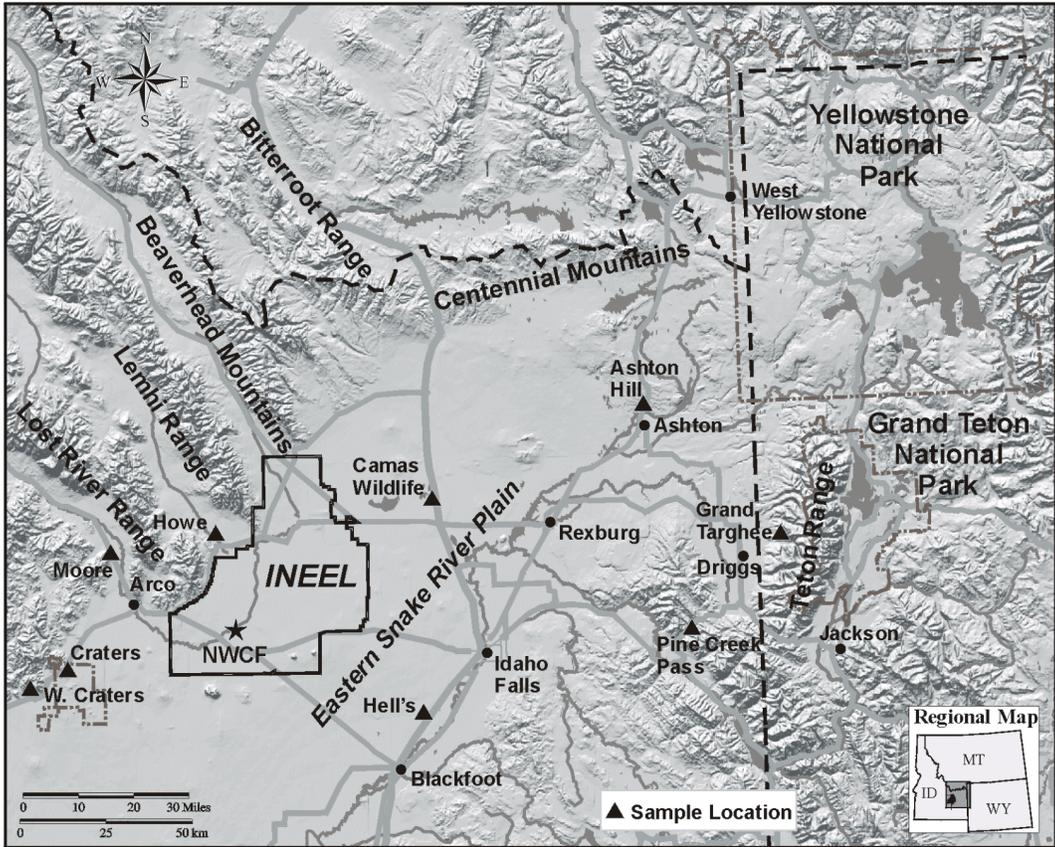


Figure 2. Regional background snow sampling locations (Pebble Creek site is 10 km south of map).

Sampling and Analytical Methods

Laboratory analysis and sample bottles were provided by the U.S. Geological Survey Wisconsin District Mercury Laboratory (WDML) in Madison, Wisconsin. The WDML is one of two full-service environmental mercury laboratories in the U.S. All sampling is done using laboratory cleaned, Hg-free sampling bottles (30 mL, 250 mL, 500 mL, and 2 L) and shoulder-length gloves; the sample bottles are kept upwind during sampling.

For snow samples, the snowpack was excavated to the ground and the snow face was cleaned using a clean lexan shovel (Hg sticks to metal). At the INEEL, composite samples of the entire snowpack thickness (typically about 20 cm) were collected using special precleaned 500 mL and 2 L teflon bottles. At background and glacier sites with significant (>50 cm) snowpack, a snow pit was dug, and 10-cm interval samples were collected in addition to a composite. Snow density measurements were made which are later multiplied by the snow depth to determine the snow water equivalent (SWE) at each location (SWE is equivalent to the mass [kg] or depth of water [mm] per unit area). After sampling, the bottles were double-bagged, placed into a cooler, and shipped frozen to the WDML.

Rain samples were collected in portable collectors consisting of custom-made 20 L teflon bag liners inside 55-cm-wide × 37-cm-long × 15-cm-high plastic storage containers (Sterilite® Clearview). The collectors were deployed at model-predicted maximum impact downwind locations on the INTEC

Grid. After the rainfall event (typically overnight), the sample (if any) was poured into a 500 mL teflon bottle. Soil samples were collected in 30 mL teflon vials after surface litter and pebbles were removed.

In the laboratory, samples were melted, acidified (to keep the mercury oxidized and in solution), and analyzed for total mercury (THg) and methylmercury (MHg).⁴ THg includes all chemical forms of Hg, including divalent Hg(II), elemental Hg(0), and methyl mercury. THg analysis was performed using EPA Method 1631, “Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS),” with modifications. MHg analyses were performed using EPA Method 1630, “Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS,” with minor modifications. For some samples, a filtered/unfiltered (FTHg/UTHg) split was analyzed, which can provide information on whether the Hg was associated with particulate or existed as a gas in the atmosphere (which provides evidence of the fallout source). Soil samples are analyzed in a similar way, except that a subsample was first taken and then digested in a mixture of nitric and sulfuric acid. The laboratory uses a rigorous QA/QC procedure, which includes duplicate analyses on every sample, spike recovery analyses at least once every 10 samples, quality control check samples, and bubbler blanks to check for background contamination (see Reference 1).

Sampling Results—Snow

A summary of the Hg snow sampling results (in ng/L) for the INEEL and background sites is provided in Table 2. For comparison, the EPA maximum contaminant level (MCL) for Hg in drinking water is 2,000 ng/L. Most of the snow samples were taken before the NWCF was started on March 15, 2000. A few background sites with late winter snowpacks (Pebble Creek, Pine Creek Pass, and Ashton Hill) were sampled after the startup date, but very limited snow sampling was possible on the INTEC grid because of the late calciner start date.

The INTEC grid sampling results conducted before calciner startup showed statistically higher Hg concentrations compared to the background sites, which was very surprising given the NWCF had not operated through the winter (see Figure 3). The following are possible reasons for these unusual results:

- Another unknown Hg source at INTEC operating during the period of snowfall (primarily in late December 1999) before the sampling (Jan 4–6, 2000)—investigated but none found. The previous calciner campaign (NWCF4) was completed in May 1999, and the High-Level Liquid Waste Evaporator was last run in July 1998.
- Soil cross-contamination during sampling—not likely because (a) the increase in concentration around INTEC was relatively uniform, which would require consistent cross-contamination with soil, and (b) the “ultraclean” sampling techniques specifically avoid contact of any sampling material with the soil surface; these methods have been previously used numerous times without any indication of cross-contamination.
- Reemission of deposited Hg in the soils around INTEC followed by absorption or hold-up in the snowpack prior to release to the atmosphere. This is a likely explanation because (a) the filtered versus unfiltered fraction (FTHg/UTHg) for the January grid samples (0.42) were higher than what has been previously measured suggesting a gaseous Hg source, (b) a mass balance calculation on the soil sampling results (see below) indicates significant reemission loss of deposited Hg from soils, and (c) soil reduction of the deposited Hg(II) and reemission as Hg(0) has been well documented, especially in high pH, low organic content soils characteristic of the INEEL. Snow and soil flux experiments are planned for FY 2001 to confirm and quantify these reemission rates.

Table 2. Summary of Hg concentrations in snow (F/U = filtered/unfiltered; M/THg = methyl/total).

Sampling Location	No. samples	THg Concentration in Snow (ng/L)			Fraction F/U THg	Fraction M/T Hg	
		High	Low	Avg.			
INTEC Grid (1/4–1/6/00, prior to calciner start):							
1 km radius	8	22	8.9	15	0.41	0.017	
2 km radius	16	15	5.5	9.3	0.45	0.019	
3 km radius	13	14	5.6	8.9	—	—	
4 km radius	12	11	4.7	7.7	0.38	0.013	
				<i>Average =</i>	10	0.42	0.02
INTEC Grid (3/17/00, after calciner start):							
1 km radius	5	141	6.4	55	—	—	
Background Sites [(A) = after calciner startup]:							
Pebble Creek	2	4.5	3.6	4.0	0.25	0.03	
Pebble Creek (A)	3	2.7	1.1	2.1	.35	0.02	
Hell's Half Acre	2	8.5	5.2	6.9	0.19	0.01	
Pine Creek Pass	13	6.8	1.5	2.2	0.33	0.03	
Pine Creek Pass (A)	6	5.9	1.7	2.2	0.26	0.01	
Ashton Hill (top)	18	12	1.8	3.3	0.42	0.02	
Ashton Hill (A)	5	5.0	2.3	3.8	0.21	0.04	
Camas Wildlife Refuge	5	3.4	1.6	2.3	0.30	0.01	
Howe area	3	6.2	1.2	3.8	0.38	0.01	
Moore area	8	7.3	0.9	3.0	0.29	0.01	
Craters of the Moon	7	3.7	1.9	2.6	0.37	0.01	
West Craters	3	4.6	2.7	3.3	0.27	0.01	
				<i>Average =</i>	3.3	0.30	0.02
<i>W. Slope Teton Range:</i>							
Tetons – 10,000 ft	6	7.8	2.56	3.5	0.31	0.004	
Tetons – 8,000 ft	4	9.3	3.6	4.0	0.28	0.04	
Tetons – 7,000 ft	3	3.1	1.7	1.7	0.33	0.01	
Tetons – 6,600 ft	4	2.6	2.0	2.6	0.19	0.01	
Teton Valley	3	6.9	2.5	4.6	0.26	0.02	
				<i>Average =</i>	3.3	0.28	0.02

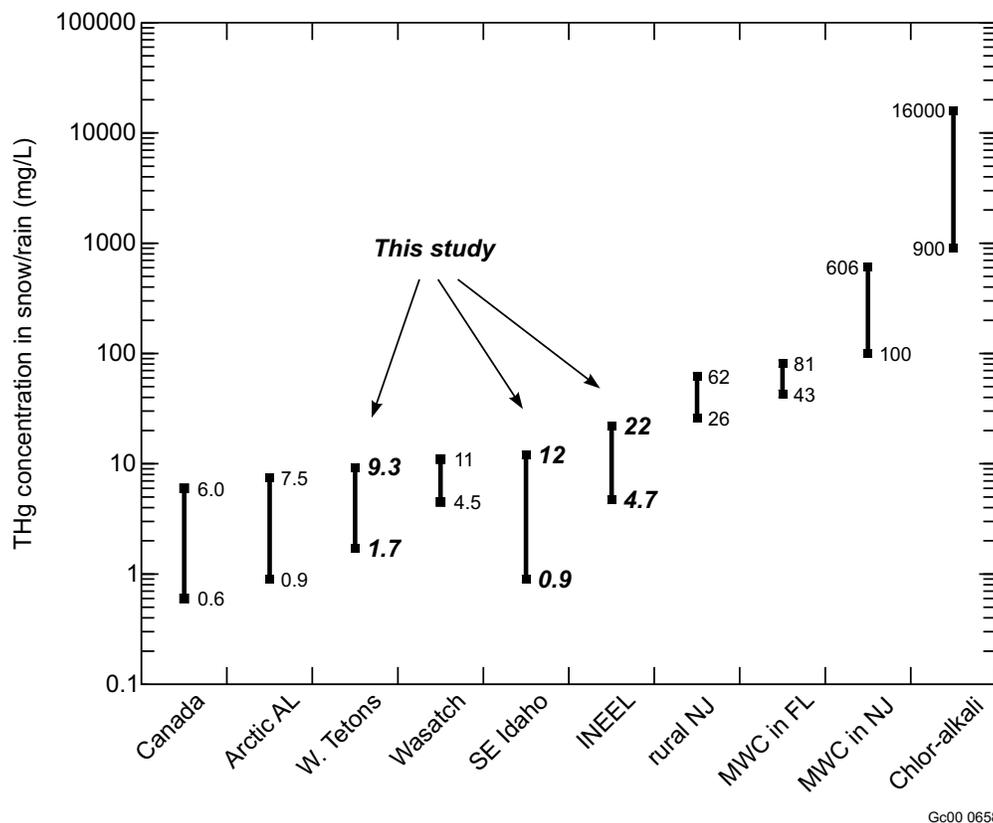


Figure 3. Comparison of snow THg concentrations found in this study (INEEL, SE Idaho, and W. slope Teton Range) with published values for precipitation (snow and rain) in other areas of the U.S. and Canada.

The INTEC grid snow sampling conducted after calciner startup indicated much higher concentrations at two locations (134 ng/L at 1 km northeast of INTEC and 141 ng/L at 1 km east-northeast). However, only a limited number of samples could be taken because of the poor snow conditions at this late date, and these samples may have been cross-contaminated with soil because of the difficulty of sampling the shallow (<2 cm) snow depth.

At background sites and the west slope of the Teton Range, snow concentrations were low (3.3 ng/L), similar to those measured in other remote low-impact locations, including arctic Alaska (0.9 to 7.5 ng/L),⁵ Ontario, Canada (0.6 to 6.0 ng/L),⁶ and in Utah’s Wasatch Range (4.5 to 11 ng/L)⁷ (see Figure 4). Concentrations in precipitation in eastern industrialized areas have been measured at much higher levels, i.e., 26 to 62 ng/L in a rural New Jersey area,⁸ 606 ng/L near a municipal waste combustor (MWC) in New Jersey, and 16,000 ng/L near a chlor-alkali plant in an urban residential area.⁹

Snow sampling on the Upper Fremont Glacier, Wind River Range, Wyoming was successfully completed May 1–8, 2000. Twenty 500-mL snow samples were collected from the full winter snowpack (two replicate pits 2.3 m deep) on the glacier at 13,200-ft elevation. The analytical results indicated very low mercury concentrations (0.3 to 0.9 ng/L) relative to the expected background concentration in precipitation in this region (1 to 3 ng/L). The laboratory analytical QA procedures were verified, and the results were found to be valid. These low results are currently being investigated but may be due to excessive Hg volatilization in the snowpack driven by the unusually dry winter (and therefore relatively old age of the snow sampled) and the high solar radiation conditions that existed during the months prior to sampling (a reemission driver).

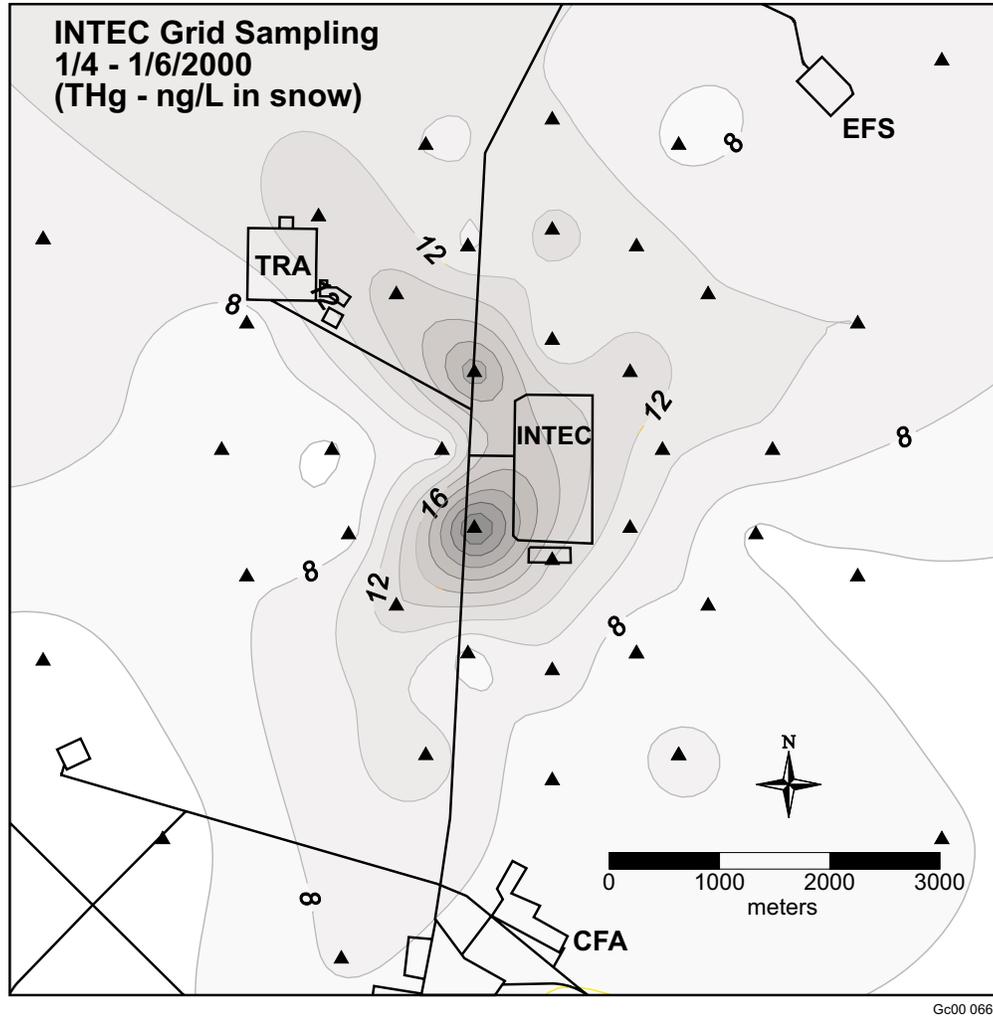


Figure 4. THg concentrations in snow (ng/L) sampled on the INTEC 5-km grid prior to startup of the calciner (3/15/00).

Sampling Results—Rain

Snow sampling on the Inilchek Glacier in Central Asia was successfully accomplished during the first two weeks of July 2000 in collaboration with a USGS glacier ice-coring expedition. Fifty snow samples from three 3-m-deep snow pits (two to three seasons of snow) were obtained and are currently being analyzed. These samples will help fill important data-gaps on global cycling of Hg in remote locations. The EPA Office of International Activities expressed interest in this work during a May 25, 2000 conference call.

Only three significant rain events occurred before shutdown of the calciner at the end of May 2000. Six rain samples were successfully obtained at three locations on the INTEC grid during one of these events (May 17, 2000). Two of these locations were chosen to be directly in the plume path (northeast at 1 and 2 km) and one was taken in the cross-wind direction (northwest at 1 km). Concentrations ranged from 14 to 20 ng/L in the plume path to 11 ng/L in the cross-wind direction. The demonstration of a successful collector design that is inexpensive and easily deployed is considered the most important result from these sampling activities.

Sampling Results—Air

Some limited air sampling was performed on the INTEC 5-km grid while the calciner was operating using a Bios AirPro portable air sampler (1 L/min) and goldtraps (gold-coated silica sand in a glass tube). The results ($n = 3$, $u = 2.23 \text{ ng/m}^3$) were within the global background range (1 to 3 ng/m^3) expected for this region. These results are not unexpected since goldtraps only trap elemental Hg(0), and emissions from the calciner are believed to be primarily in the divalent Hg(II) state.

Passive integrated mercury samplers (PIMs), still in a developmental stage, were obtained without cost through collaboration with the USGS Columbia Environmental Research Center (CERC) in Columbia, Missouri. Three of these units were deployed for 25 days on the INTEC sampling grid during calciner operations. Analytical results showed a blank contamination problem (from the stainless-steel shipping cans), and the results were not considered valid. The CERC has fixed the problem and may provide more PIMs (in different Hg-free shipping containers) for INEEL deployment in the future.

Sampling Results—Soil

Before comprehensive INTEC grid soil sampling, two experiments were conducted in July 2000 to determine Hg distribution in the soil around INTEC. The first experiment examined Hg concentration as a function of soil depth at a high-fallout location 1 km northeast of INTEC. Twenty-four soil samples were taken at 1-in. depth intervals down to 4 in. using a custom-made soil horizon sampler (borrowed from the State of Idaho INEEL Oversight Program). Results showed that Hg soil concentrations decrease about 10%/in. of soil depth (see Figure 5) and that overall soil concentrations near INTEC are low relative to background levels published for similar soils in other regions in the U.S. (50 to 60 ng/g).

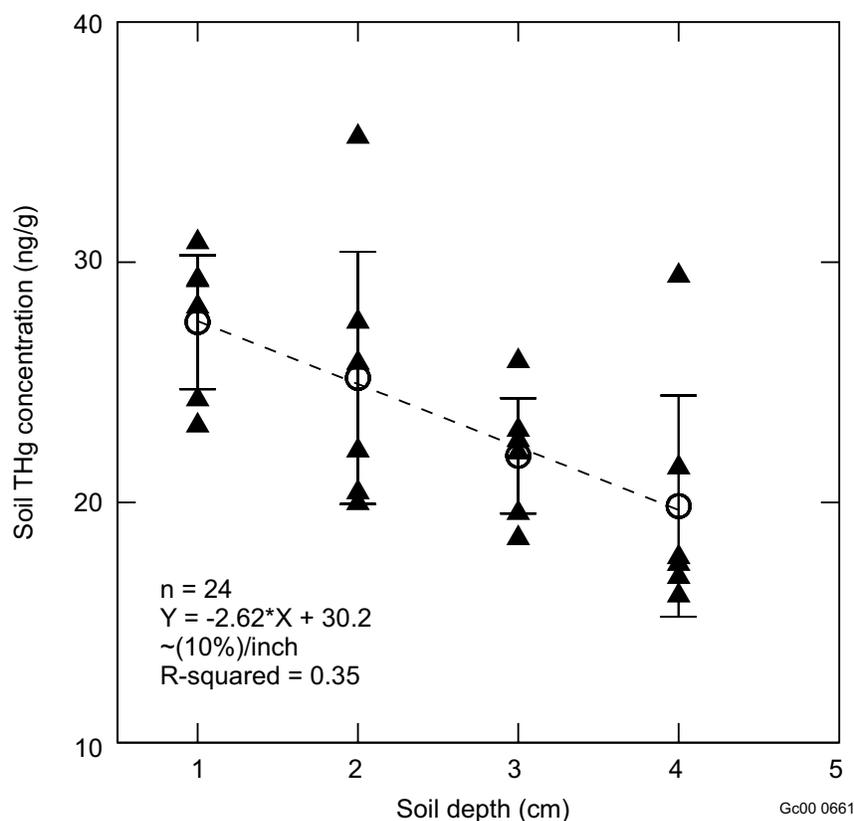


Figure 5. THg concentrations in soil near INTEC decreased approximately 10%/in. with depth.

The second experiment examined the variability of surface soil Hg concentrations as a function of vegetation type/cover and soil runoff features (rise vs. depression). These results (see Figure 6) show (a) Hg soil concentrations under shrub (sagebrush and rabbitbrush) canopies are a factor of 2 higher ($p < 0.05$) than soil concentrations in grassy or bare areas, likely due to fixation by the higher organic matter content of soils there, and (b) Hg soil concentrations in depressions are a factor of 2 higher than in adjacent elevated areas, likely due to runoff.

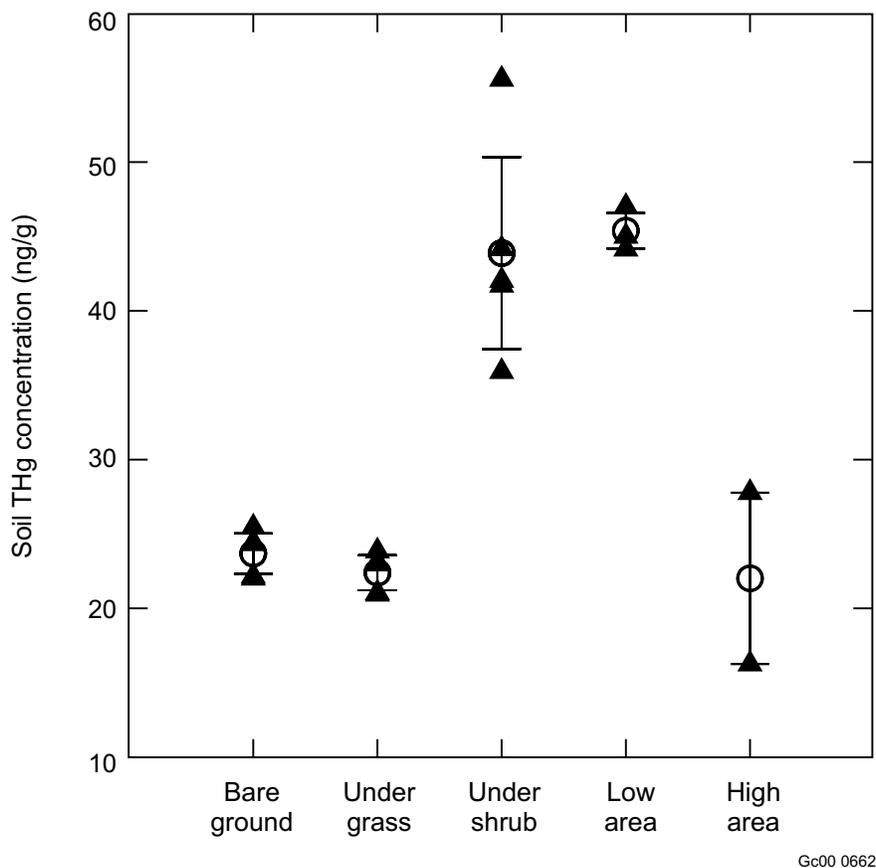


Figure 6. THg concentrations in soil under shrubs and in depressions were found to be a factor of 2 higher ($p < 0.01$) than concentrations in soil under grass, with no vegetation, or in elevated areas.

Comprehensive soil sampling results on the INTEC grid (see Figure 7) showed very low Hg concentrations overall compared to similar soils across the U.S. and a slight increase ($p < 0.05$) in concentrations within 5 km of INTEC (the “halo” in Figure 7). An estimate of the total calciner Hg load in the soil around INTEC and a mass balance of calciner Hg emissions over its 37-year operating history was made by (a) integrating surface soil concentrations across the 5-km grid (where most of the fallout was observed) and out to a conservative range of 20 km using Surfer[®] 7^a kriging and volume tools and a conservatively-low background level of 7 ng/g; (b) repeating this process at 1-cm depth layers, reduced in concentration by 4% per cm (from the soil depth experiment), down to “0” integrated concentration; and (c) summing the calculated Hg mass in the 1-cm layers. The results show a total surface soil load near the facility of 37–300 kg which is a small fraction (3–20%) of the estimated cumulative 37-year emissions from the calciner (1,500 kg).

a. Golden Software, Inc., Golden, Colorado 80401; www.goldensoftware.com

ACCOMPLISHMENTS

Samples of snow (n = 130), rain (n = 6), soil (n = 103), and air (n = 5) were successfully collected on the INEEL and at 11 regional background sites from January through March 2000. Snow samples were successfully obtained from the Upper Fremont Glacier, Wyoming, in May (n = 20) and the Inilchek Glacier, Central Asia, in July (n = 50). This sampling required development and successful implementation of ultraclean sampling techniques necessary for consistent preservation of ambient Hg at parts-per-trillion levels, and successful and safe field operations in harsh winter conditions, even at some high-altitude locations. All samples except one passed rigorous laboratory QA/QC procedures, which included duplicate analyses on every sample (<10% variation), spike recoveries and quality control check samples every 10 samples ($\pm 10\%$), and bubbler blanks for background correction.

The major conclusions from this field research are as follows:

- Mercury concentrations in precipitation fallout are very low both on the INEEL and regionally. The highest concentration found on the INEEL during calciner operations was 141 ng/L, less than one-tenth the EPA's MCL for Hg in drinking water (2 ppb or 2,000 ng/L). Most concentrations on the INEEL were significantly lower. Concentrations at regional background sites were much lower and similar to the background fallout rate (3 ng/L) expected for this region. This background fallout rate is as low or lower than anywhere else in the U.S.
- Most of the Hg in the calciner emissions, which is almost 100% Hg(II), is deposited within 10 km of the stack, based on reconnaissance field sampling and model validation work done in 1999.¹⁰
- Mercury concentrations in surface soil near INTEC (15 to 20 ng/g) increase slightly at distances closer than 5 km, indicating a contribution from the calciner. However, the concentrations measured at all locations near INTEC are very low compared background Hg concentrations in similar soils around the U.S. (50 to 70 ng/g).
- A mass balance of the soil sampling data near INTEC indicate 40 to 300 kg of Hg from calciner emissions remain in the surface soil. This is estimated to be 3 to 20% of the cumulative 37 years of Hg deposition from the calciner (est. 1,500 kg).
- It is likely that most of the Hg fallout from calciner operations was initially deposited as Hg(II) close to INTEC, subsequently reduced in the soil to Hg(0), and then reemitted to the atmosphere where it would have become part of the global atmospheric Hg pool. Elemental Hg(0) does not readily deposit to the ground, and may be transported long distances in the atmosphere before a small fraction of it is oxidized and subsequently deposited on the ground. Confirmation and quantification of snow and soil Hg reemission losses on the INEEL will be pursued using flux chamber measurements in FY 2001.

Future Work

Future work includes continued precipitation and soil sampling on the INEEL and regionally, and new efforts on reemission flux measurements and aquatic ecosystem sediment sampling.

To better understand Hg cycling on a global scale, additional parameters affecting Hg speciation and transport between various environmental compartments (air, soil, sediment, and biota) may need to be

investigated. One area currently thought to be important, but of which very little is known, is the effect of soil microorganisms and biochemistry.

REFERENCES

1. Environmental Protection Agency, *Mercury Study Report to Congress (Vols. I-VIII)*, <http://www.epa.gov/oar/mercury.html>, EPA-452/R-003 through 010, December 1997.
2. Environmental Protection Agency, "Mercury Research Strategy," *NCEA-I-0710 Workshop Review Draft*, November 1999.
3. M. L. Abbott, K. N. Keck, R. E. Schindler, R. L. VanHorn, N. L. Hampton, and M. B. Heiser, *Screening Level Risk Assessment for the New Waste Calcining Facility*, INEEL/EXT-97-00686 Rev. 5a, May 1999.
4. M. L. Olson and J. F. DeWild, "Techniques for the Collection and Species Specific Analysis of Low Levels of Mercury in Water, Sediment and Biota," D. W. Morganwalp and H. T. Buxton (eds.), *U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting*, Charleston, SC, USA, March 8–12, 1999, Volume 2 of 3—*Contamination of Hydrologic Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report*, 99-4018A, 1999, pp. 191–201.
5. E. Snyder-Conn, J. R. Garbarino, G. L. Hoffman, and A. Oelkers, "Soluble Trace Elements and Total Mercury in Arctic Alaskan Snow," *Arctic*, 50, 1997, pp. 201–215.
6. V. L. St. Louis, J. W. Rudd, C. A. Kelly, and L. A. Barrie, "Wet Deposition of Methylmercury in Northwestern Ontario Compared to Other Geographic Locations," *Water, Air, and Soil Pollution*, 80, 1995, pp. 405–414.
7. D. D. Susong, M. L. Abbott, and D. P. Krabbenhoft, "Reconnaissance of Mercury Concentrations in Snow from the Teton and Wasatch Ranges to Assess the Atmospheric Deposition of Mercury from an Urban Area," Abstract H12b-06, *Eos, Transactions of the American Geophysical Union*, 80, 1999, p. 46.
8. A. Greenberg, I. Wojtenko, H. Chen, S. Krivanek, J. Butler, J. Held, P. Weis, and N. Reiss, "Mercury in Air and Rainwater in the Vicinity of a Municipal Resource Recovery Facility in Western New Jersey," *The International Symposium on Measurement of Toxic and Related Pollutants, Durham, North Carolina, May 8, 1992*.
9. P. J. Temple, and S. N. Linzon, "Contamination of Vegetation, Soil, Snow, and Garden Crops by Atmospheric Deposition of Mercury from a Chlor-Alkali Plant," in D.D. Hemphill (ed.), *Trace Substance in Environmental Health – XI*, University of Missouri, Columbia, Missouri, 1977, pp. 389–398.
10. M. L. Abbott, D. D. Susong, and D. Krabbenhoft, "Comparison of Mercury Measurements in Snow with ISCST3 Model-Predicted Deposition Near an Industrial Emission Source in Southeastern Idaho." *Air & Waste Management Association International Conference on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina, September 13, 2000*.

Ion Mobility Spectrometry for Environmental Monitoring and In Situ Measurement of Hazardous Organics

Enhancing Environmental Chemical Data Gathering and Analysis
in the Field

David A. Atkinson, Robert G. Ewing, and Keith A. Daum (INEEL); Herbert H. Hill (Washington State University); Gary Eiceman (New Mexico State University)

SUMMARY

Environmental monitoring scenarios often require considerable chemical analyses to monitor contaminant levels and define transport and exposure potential. Long-term stewardship of federal lands entails extensive chemical monitoring and characterization. The costs and operational complications involved in this process can be staggering. Advanced chemical analysis technologies are needed to reduce the burden of characterization and monitoring. Ion mobility spectrometry (IMS) is a field proven, sensitive, rugged, portable detection device able to detect a wide variety of trace organics. Ion mobility spectrometry characterizes chemicals by their behavior in an electric field. Many difficult environmental monitoring challenges involve getting high quality analytical field data with high sample throughput. IMS is well suited to this, and can provide high speed, high quality data while deployed at the problem site. The flexibility of the IMS inlet can be exploited with a variety of analytical sample types including ambient air samples, soil gas samples, groundwater samples, and organic waste samples. This task further develops IMS technology such that it will become a tool of choice for onsite analysis.

This research task focuses on developing IMS for onsite/in situ environmental detection in soil and water, and in more efficient detection of trichloroethane (TCE), 1,1,1-trichloroethane, and chloroform—contaminants of significant interest at the INEEL and across the DOE complex. Exploiting the capability of IMS should create a powerful tool for EM that is faster, cheaper, and more accurate than existing detection and analysis methods.

TASK DESCRIPTION

This task had three major subtasks to perform this fiscal year, which focused on using IMS as an environmental monitor with emphasis on onsite or in situ monitoring.

Monitoring Volatile Organic Transport Using a Miniature Field Asymmetric Waveform IMS Sensor

The first subtask was to develop a miniature field asymmetric waveform IMS (FAIMS) sensor for monitoring the transport of volatile organic vapors through soil. FAIMS is a relatively new technique, which is a variation of traditional IMS. FAIMS operates with a high-voltage, high-frequency asymmetric waveform between parallel plates. A stable ion trajectory between these two plates is established with a compensating direct current (dc) voltage. Ions with varying mobilities under these conditions require different compensating voltages to obtain a stable trajectory and reach the detector. Thus, a spectrum is obtained by scanning this compensation voltage and monitoring ion current. The advantages of this sensor over those of conventional IMS are sensitivity gains achieved due to the absence of an ion shutter, and anticipated reduced instrument size, since the actual sensor is approximately 25 mm in diameter. Current

size limitations are due to supporting electronics. With the sensitivity and size of this sensor, it is envisioned as an ideal tool for monitoring specific volatile organic compounds downhole. This monitoring could allow for mapping of the underground transport of organic vapors and provide data to support transport modeling efforts. For this subtask, the INEEL collaborated with New Mexico State University to develop the proof-of-concept sensor for soil monitoring.

Until recently, miniaturization of IMS drift tubes had been considered unpromising since conventional ion injection schemes lead to losses in resolution with small drift tubes; also, unacceptably high noise is created through microphonics in the aperture grid-detector. This noise obscures the extra low signal levels found in drift tubes of reduced dimensions. In spite of these barriers, a few small drift tubes have been successfully demonstrated on the miniature scale by several teams (U.S. Army at Edgewood Research Development and Engineering Center¹ and Oak Ridge National Laboratory²). The concept of a microscale drift tube was proposed by a team in Germany,³ and New Mexico State University researchers described a micro-machined drift tube based on the Radio Frequency (RF)-IMS method in 1999.⁴ In this microanalyzer, the drift region had rectangular dimensions of $30 \times 10 \times 20$ mm. In the RF-IMS design, the ion shutters, voltage dividers, and aperture grids are eliminated from the drift tube, which greatly simplifies the complexity of drift tube fabrication. Ions are carried through the drift region using a flow of gas and ion trajectories between parallel plates are proscribed by ion interactions with a high-voltage, oscillating, electric field. Mobilities become field dependent under the RF field in contrast to the low-field regimes used in conventional IMS drift tubes. A second electric field, a weak dc voltage, is superimposed on the high-voltage RF waveform. The dc field may be between 0 and 400 V/cm and the peak amplitude of the RF field is $\sim 25,000$ V/cm with a frequency of 1.2 MHz. The fields are said to be asymmetric since the portion of the RF waveform at high voltage is shorter than that at low voltage. These fields are applied perpendicular to the carrier gas flow direction in the drift region, and only certain ion species will reach the detector at the end of the drift tube, as governed by the dc field for a given RF field. Previous studies on the role of the high fields on ion behavior⁵⁻¹⁰ have illustrated that the RF method is a plausible tool to characterize organic ions of all sizes.

In a high field RF-based drift tube, ions are transported through a drift region by a carrier gas flow while an RF electric field is applied to plates in the drift region that are spaced by 10 mm. This field is 90 degrees to the gas flow and causes the ions to oscillate in a direction transverse to the carrier gas flow. The amplitude of the RF waveform under high field conditions is $>10,000$ V/cm and the ion is moved rapidly toward the top plate (or electrode). In contrast, the ion under the low field portion of the RF waveform (~ 100 V/cm) moves toward the bottom plate at a comparatively slow velocity, which draws the ion toward one plate by a net amount Δh for each RF period. The average value of Δh for an ion species is determined by the duty cycle of the RF field and the field dependence of the mobility $K(E)$. Thus, the total displacement of the ion in space is $n\Delta h$ as governed by the number of RF periods, wherein ion separation occurs, which can also be understood as a differential mobility analysis ($K(E) - K_0$). The resultant motion in the drift region appears to be specific to each ion species, though this requires further investigation.

Only ions with a total transverse displacement less than the drift region width will reach the detector; all other ions will collide with drift tube wall (or plates). These ions are neutralized or annihilated and removed from the drift region in the gas flow. Ions of a given kind can be kept from striking the plates (allowing a stable passage to the detector) by applying a low voltage dc field to the ion plates in opposition to the net RF-induced transverse motion of the ion. A sweep of compensation voltage will provide a measure of all the ions in the analyzer and results in a RF high-field mobility spectrum. In traditional low field IMS, ion mobilities are reasonably well described through the Mason-Schamp equation¹³ and reduced mobility constants (K_0) are related to reduced mass and cross-section areas for ion-molecule collisions where ion mobilities are independent of electric field. In contrast (part of the time for ion drift), the ion experiences high fields and mobilities that are field dependent. The RF-field

interacts with ions in ways that allow ion separations based on ion-molecular interactions, which are not available for use in low field (or time-of-flight) mobility spectrometers. Thus, some intractable challenges for ion separation in time-of-flight IMS analyzers are easily resolved in the RF-based drift tube.

The setup and testing of the system for this subtask was done by Professor Gary Eiceman's laboratory at New Mexico State University, under subcontract to the INEEL. The initial studies looked at the environmentally important hydrocarbons benzene, xylenes, and toluene, as well as a suite of chlorinated hydrocarbons. Figure 1 illustrates toluene response at sub-ppm levels for a number of different concentrations. Photoionization is used, since hydrocarbons such as toluene do not respond well with traditional beta decay driven ionization processes. The use of photoionization can provide a response to a number of analyte groups that respond poorly in traditional IMS. Figure 2 illustrates the area and height response curves to the various toluene concentrations. The response is strongly linear over the concentration range studied. Figure 3 demonstrates the separation power of the prototype FAIMS system. Mixtures of benzene/acetone as well as toluene/acetone were evaluated. Baseline resolution between all components was achieved. This is a difficult separation in conventional time-of-flight IMS, but easily resolved using the FAIMS technique. IMS is traditionally considered a fairly low resolution technique (especially in comparison to other analytical techniques such as gas chromatography (GC) and mass spectrometry), however, the FAIMS device offers much promise in this area. Figure 4 further illustrates the separation power of the FAIMS. An analysis of a mixture of the three xylene isomers is shown for both conventional time-of-flight IMS and the FAIMS. The rightmost peaks in the conventional IMS system correspond to the xylene isomers; it can be seen that no separation is achieved. The peaks to the left in the conventional IMS spectrum correspond to the reactant ions, which are developed from the ionization of the air bath gas. In the FAIMS spectra, the m-xylene isomer is well resolved from the ortho- and para-isomers. There is no separation between the ortho- and para-isomers. Given that IMS separates based on the charge, size, and shape of molecules through collision processes, it is no surprise that these isomers are difficult to separate.

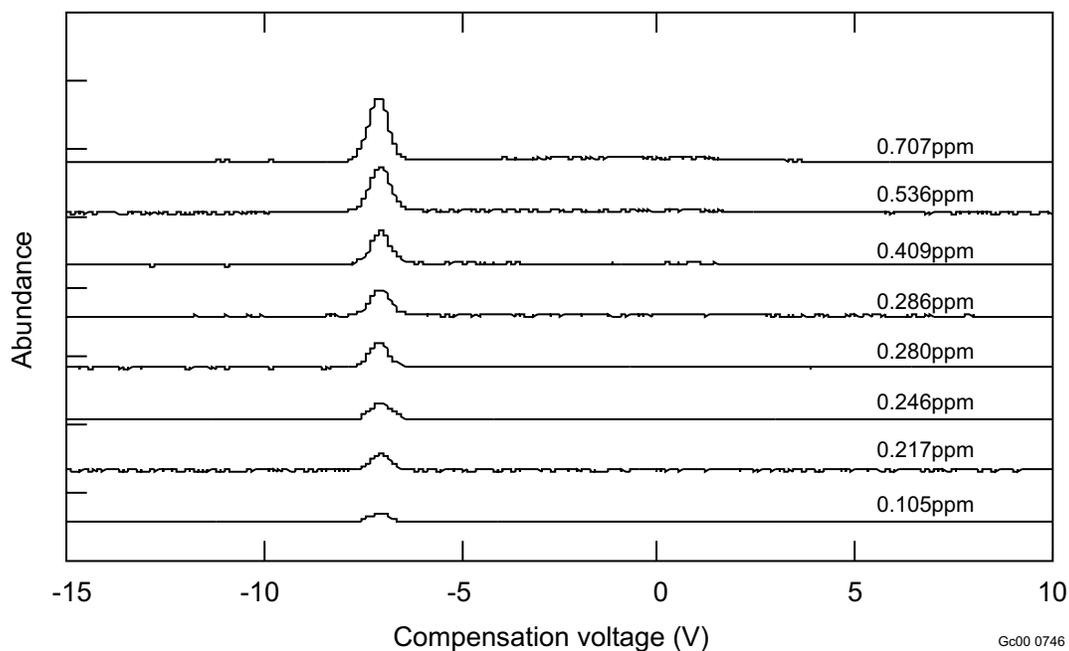


Figure 1. FAIMS spectra for toluene at varying concentrations.

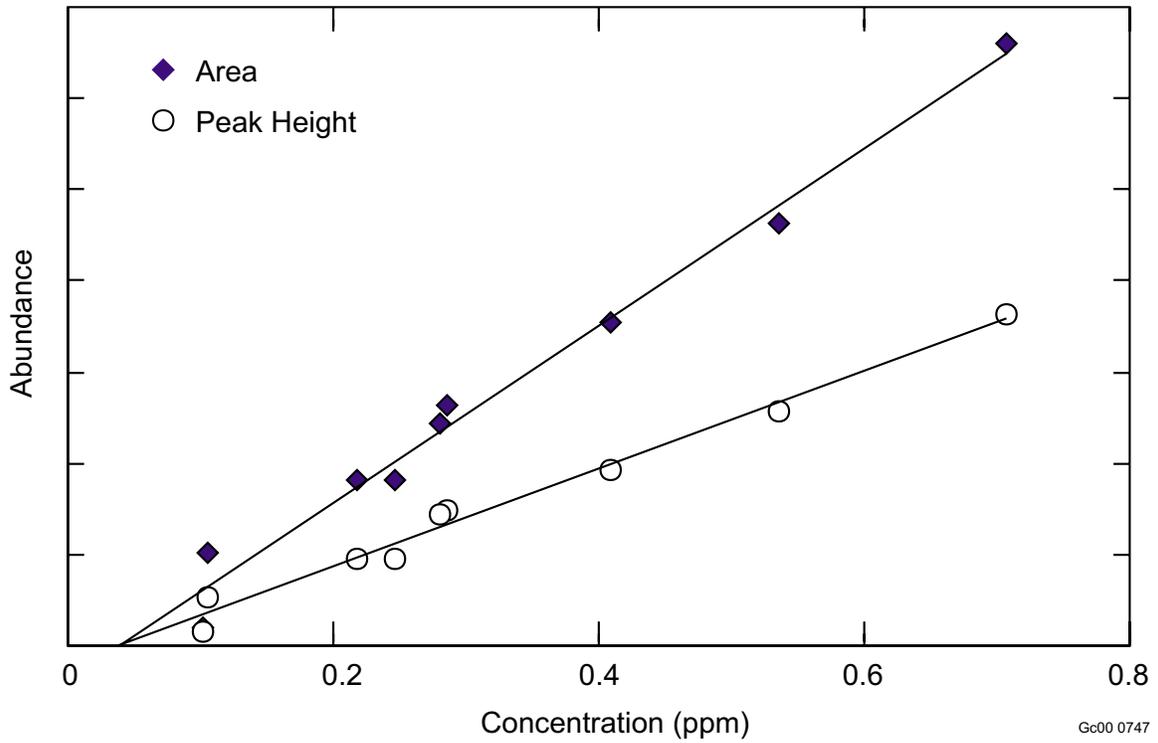


Figure 2. Toluene response curves.

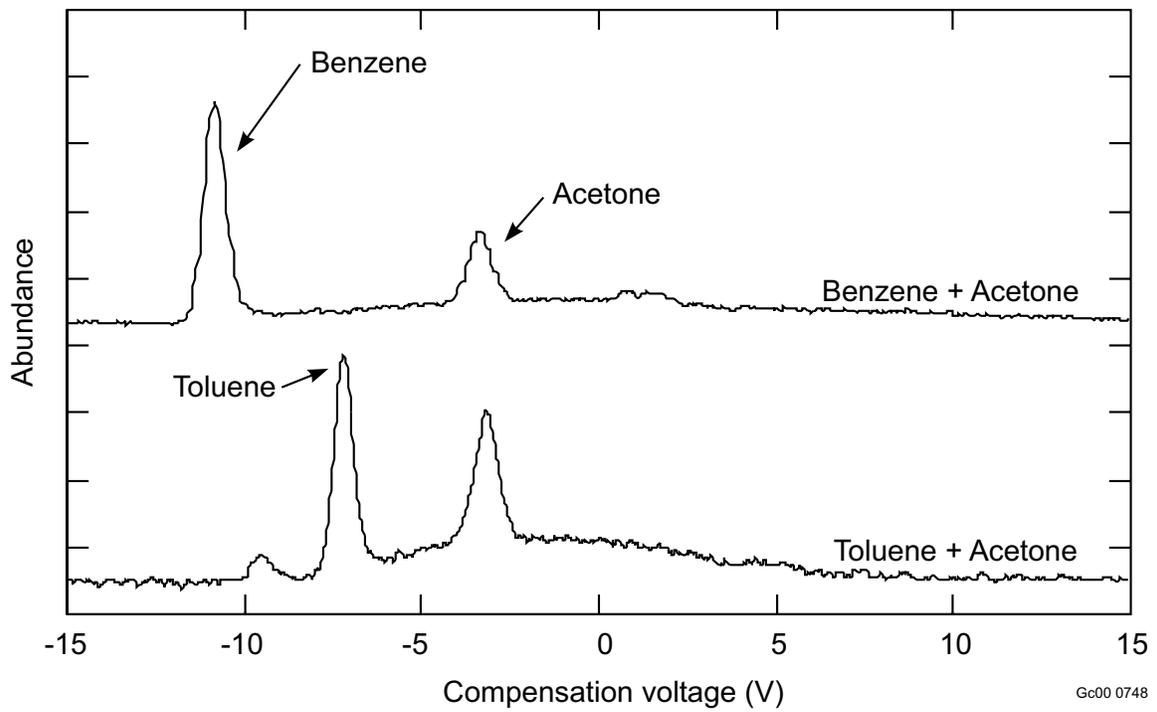


Figure 3. Separation of benzene/acetone and toluene/acetone mixtures.

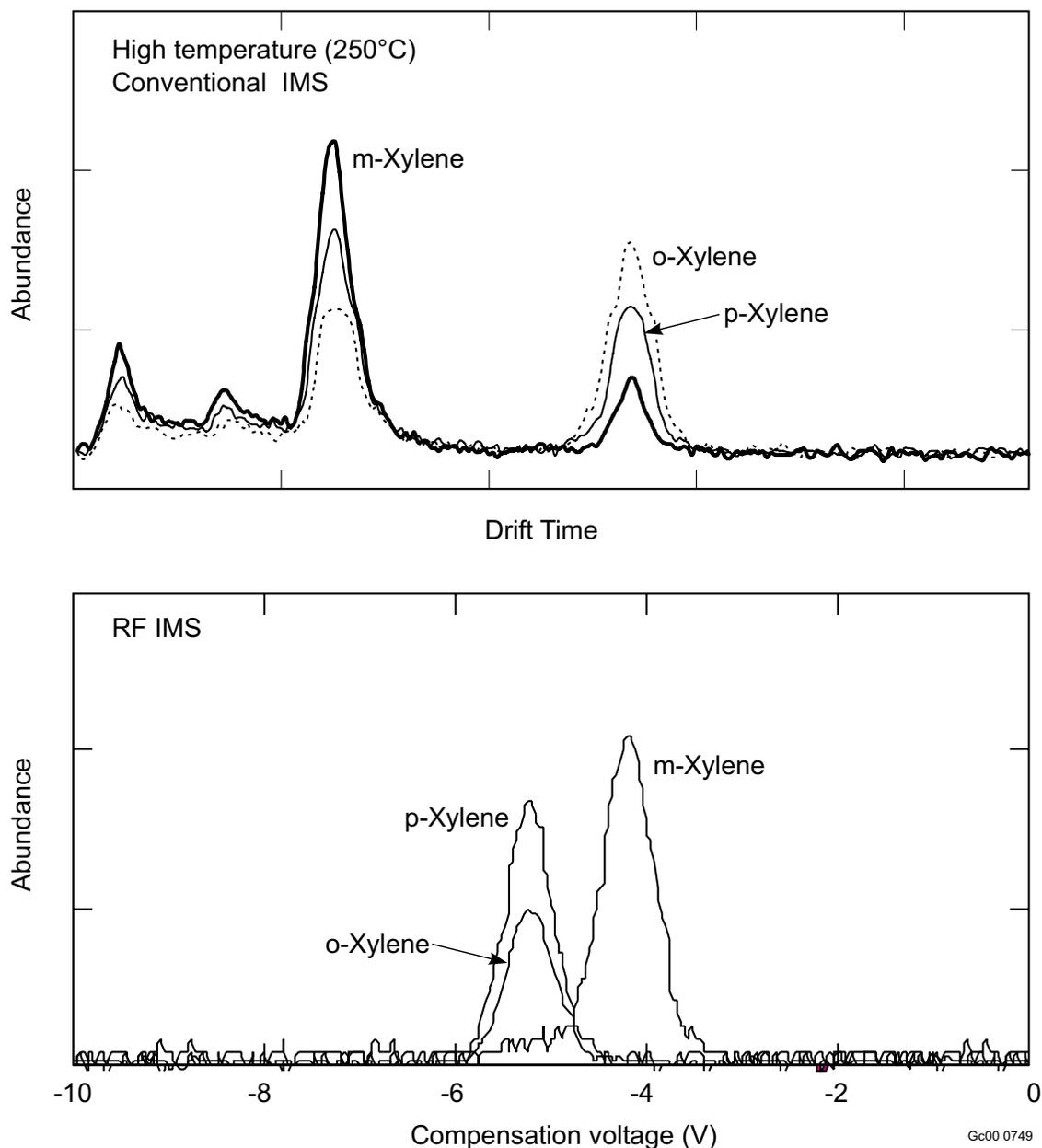


Figure 4. Comparison of xylene isomer separation in different IMS systems.

In Figure 5, the separation is shown for 13 volatile halocarbons using a gas chromatograph (GC) coupled to the FAIMS. The chromatogram on the right shows the resolution of the mixture into a solvent peak (retention time of 100 s) and 13 peaks. Mobility scans for the FAIMS analyzer were obtained continuously throughout the GC elution profile and were obtained for both positive and negative ions. Generally, halocarbons have been regarded as sensitive only in the negative polarity, and the ionization processes in atmospheric pressure chemical ionization sources generally lead to dissociative electron capture (Cl^- or Br^-). Historically, positive ion response toward halocarbons has been considered unpromising. The results here are remarkable and show instead that positive ion RF mobility scans were full of information and were characteristic of each chemical. In the figure, the reactant ion peak is shown

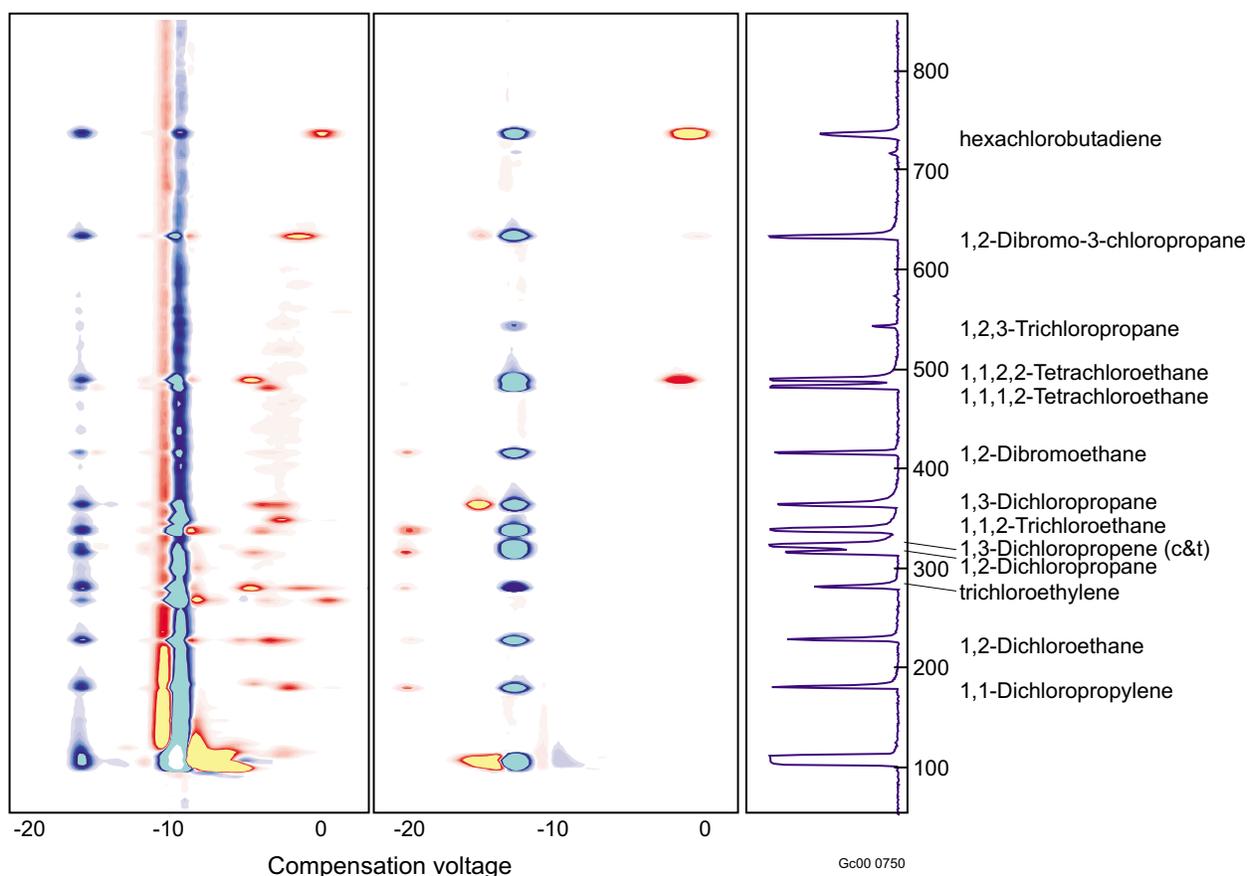


Figure 5. GC/FAIMS data from 13 chlorinated hydrocarbons.

at -9V ; this is understood as a hydrated proton. Peaks to the right of this (-8 to $+1$ V) are product ions that have not yet been identified. Nonetheless, the presence of unique retention times and characteristic positive ion scans for many, if not all, of the halocarbons illustrate that the FAIMS has a strong potential as an in the field analyzer for chlorinated hydrocarbon species. The next focus of the work will be to demonstrate the effectiveness of the technique in actual field trials, including the performance of measurements with the sensor cell down hole, as well as optimize the system to provide the best performance for environmental analytes of concern in the field.

Electrospray Ionization/IMS for Surface and Groundwater Monitoring

The second subtask involves the development of an electrospray ionization front-end to ion-mobility spectrometry for a high-speed detection system for organic pollutants in environmental water samples. The electrospray ionization source can directly inject environmental water samples into an ion mobility spectrometer system for analysis. This combination provides a sensitive, rugged, and high throughput direct water analysis system that requires essentially zero sample preparation. As well as organic pollutants, ionic species of environmental interest, such as nitrate, nitrite, sulfate, chloride, and others, can be monitored. This device can be packaged into a portable format, for deployment in the field. The INEEL and Washington State University (WSU) collaborated on the assembly of a prototype instrument from existing WSU equipment.

The detection and quantification of polar and ionic molecules such as inorganic ions, explosives, chemical warfare agents, and pesticides from soil and groundwater samples is a difficult and expensive analytical procedure. Representative collection of the sample, transportation of the sample to the analytical laboratory, separation of the analyte from the matrix, concentration of the analyte, isolation of the analyte from other contaminants, and detection of the analyte for identification and quantification are complex procedures currently required for the analytical determination of many important environmental compounds.

Collection of a representative sample is important for the characterization of a contaminant area. When samples have to be transported back to the analytical laboratory before they are evaluated, decisions about remediation and safety must be postponed for hours, days, or even weeks. When samples must be collected in the field and analyzed in the laboratory, an extensive set of samples is required to obtain a detailed description of the contaminated site while reducing the necessity for iterative sampling and analysis. Yet the iterative sampling and analysis approach to site characterization permits a more thorough understanding of the extent of contamination. A field-based method of analysis would permit the iterative approach for characterization of a contaminated area. While field-based analytical methods exist for volatile and nonpolar organic compounds, they do not exist for polar and ionic compounds.

Advantages, other than the reduction of analysis time, are cost and sample integrity. Not only do the processes of collection, shipping, and storage of samples generate additional costs, they also provide opportunities for the analyte to decompose or degrade and for the sample to become contaminated with extraneous material, leading to analytical errors. Field-based methods reduce the possibility of analyte degradation and sample contamination, thus improving the integrity of the analysis.

The lack of field-based methods for detecting polar and ionic compounds has resulted in a poor understanding of these compounds in soil and aqueous environments. The information that is available for these compounds has been obtained at considerable expense. The reasons that rapid, field-based methods for polar and ionic compounds do not exist are complex, but are primarily due to the water solubility of these compounds. Because of the polar and ionic nature of these compounds, they are difficult to extract from aqueous samples. GC has been developed for field analysis, but is best suited for nonpolar, volatile compounds. Samples dissolved in water are difficult to inject efficiently onto a gas chromatographic column. One approach for the determination of polar and ionic compounds is to derivatize the analyte by blocking the polar moiety, decreasing the solubility of the compound in water and increasing its volatility for GC analysis. The most common approach for the determination of polar and ionic compounds is by liquid chromatography. Liquid chromatographic methods are slow, cumbersome, and not sufficiently sensitive for many field applications.

Initial studies of ions in aqueous based standards focussed on cations, due to the stability and ease of development in the positive mode. Negative mode electrospray has proven to be more difficult, and less stable. Thus, it was more expedient to develop the initial methodology in the positive mode for cations before moving over to explore anions. After the initial setup of the electrospray IMS system, the instrument parameters were adjusted to provide optimal response to the cations being studied. Figure 6 illustrates the electrospray IMS response to lanthanum and strontium chloride. The bottom spectrum in the figure is a mixture of the two salts. The product ion peaks in the mixture match the individual peaks from the standards, demonstrating the utility of the technique in separating cations with a very short analysis time. A similar separation using a standard method, such as ion chromatography, would take 5 to 10 minutes. This separation using IMS takes place in milliseconds. Separation of the cation species is fairly easy to achieve directly from a water sample, with minimal sample preparation.

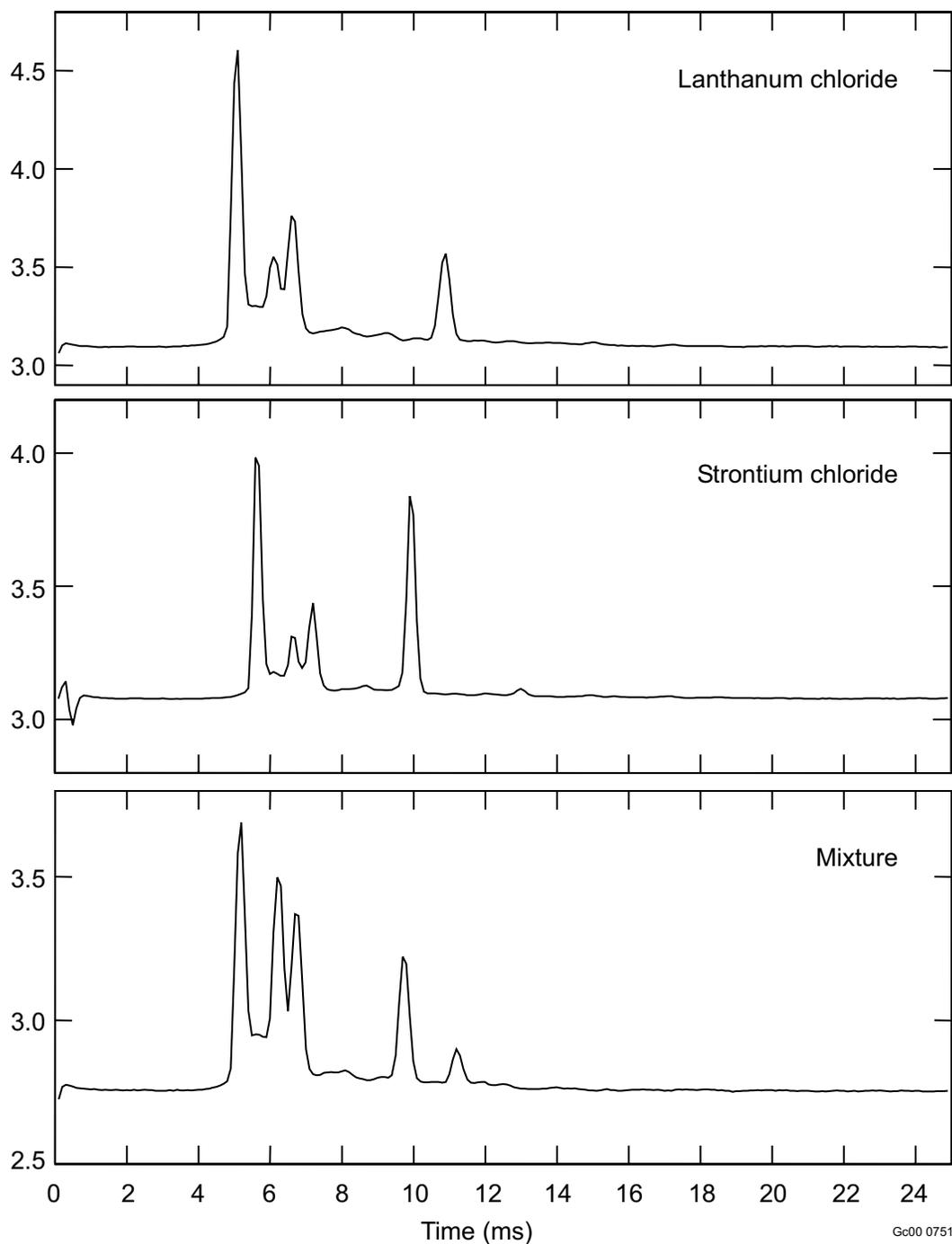


Figure 6. Lanthanum/strontium electro spray IMS spectra.

Figure 7 shows the electro spray IMS spectra for uranyl acetate and uranyl nitrate from aqueous solution. There is a difference in the product ion peak position, suggesting that the cation is different, even though both samples are uranyl species. This suggests that the counter ion has an effect on the product ion identity, most likely through effects on clustering. This phenomenon will need to be studied more in detail, including IMS/mass spectrometry data. However, the fact that an ion signal from a large cation such as uranyl ion shows the immense promise of electro spray IMS as a technique for measuring

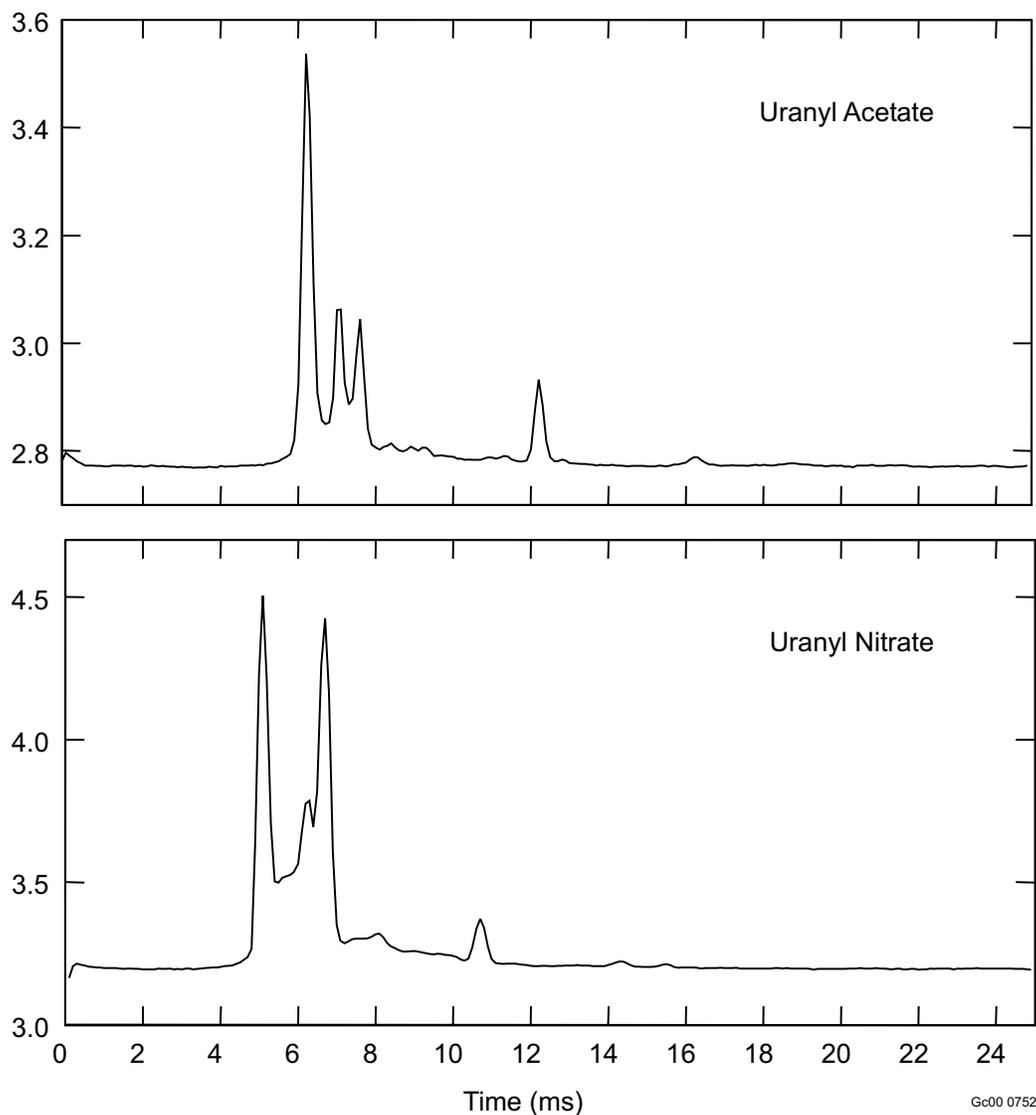


Figure 7. Electro spray IMS spectra of uranyl compounds.

specific cations directly from water solutions. Figure 8 demonstrates a separation of phosphonic acid compounds in water solution. The product ions are most likely water clustered cations from acid species.

Negative mode electro spray IMS is more difficult due to signal instabilities and electrical arcing that takes place. Figure 9 illustrates a spectrum containing a mixture of explosive compounds done via negative mode electro spray IMS. There is very good separation among the five compounds (nitrobenzene; 2,4-dinitrotoluene; 2-amino-4,6-dinitrotoluene; 2,4,6-trinitrotoluene; and 1,3,5-trinitrobenzene). Again, IMS provides a high speed (millisecond) separation that would take up to 20 minutes via a standard method, such as EPA 8330, and high performance liquid chromatography based method.

The utility of the electro spray IMS has been demonstrated for cations and negative mode molecules in water solutions. The next goal is to demonstrate the effectiveness of the technique for anionic species in water, specifically nitrate and nitrite. Beyond optimization of the technique for aqueous anions, field testing and demonstration will take place.

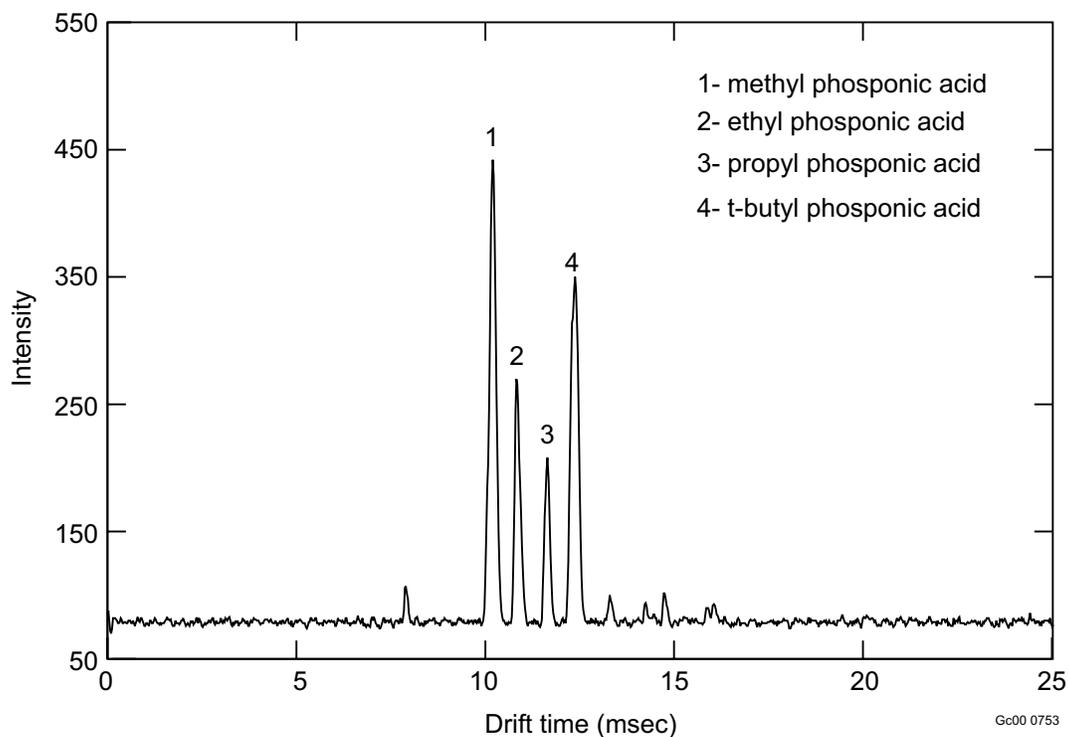


Figure 8. Electrospray IMS spectra of phosphonic acids.

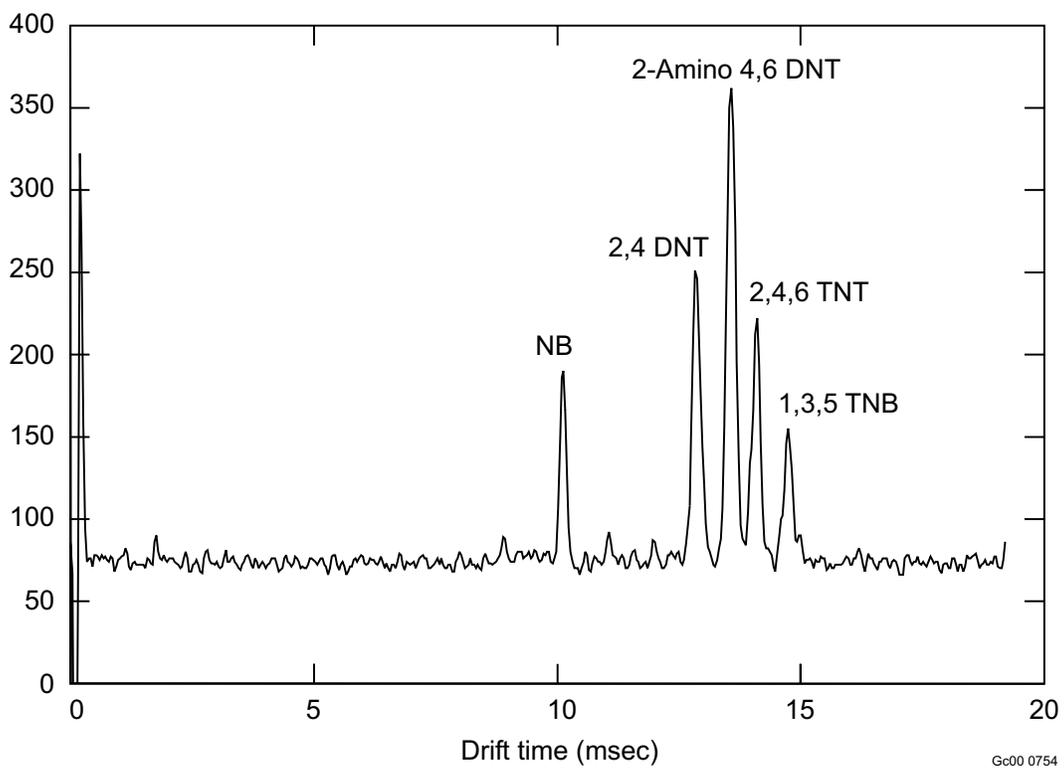


Figure 9. Negative mode electrospray IMS of explosive compounds in water.

Speciation of Chlorinated Hydrocarbons in IMS by Gas Phase Ion Chemistry Manipulation

The third subtask involves the speciation of chlorinated hydrocarbons in IMS by gas phase ion chemistry manipulation. Trichloroethene (TCE), 1,1,1-trichloroethane, and chloroform are all contaminants of great interest at the INEEL site and across the DOE complex. They are found in groundwater, the vadose zone, surface water, and above ground waste sites. Ion mobility spectrometry offers an extremely promising potential field method for the detection of these compounds with large advantages over current methods. The use of IMS for direct, in the field analysis eliminates sample collection and storage and provide real time data, allowing IMS to be faster, cheaper, and probably more accurate than existing methods. The main drawback to using IMS in this application is that these compounds tend to provide only a chloride response through dissociative electron capture. Therefore, speciation among the various chlorinated hydrocarbons is difficult to impossible to achieve under standard IMS operating conditions. The key to IMS identification and quantification of these compounds is the formation of a unique molecular ion species from the contaminant of interest. Recent work with explosives at the INEEL has shown that molecular ion species not seen under standard conditions can be formed through the manipulation of the gas phase ion-molecule reaction chemistry. This subtask demonstrates the ability to form a molecular ion for chlorinated hydrocarbons. This allows the use of hand-held IMS units for rapid screening and characterization of chlorinated hydrocarbon contamination in a variety of monitoring scenarios.

Figure 10 illustrates the use of a charge transfer agent to provide molecular ion species for 1,1,1-tetrachloroethane (1,1,1-TCA) and 1,1,2-tetrachloroethane (1,1,2-TCA). The top trace illustrates 1,1,1-TCA using standard air based ionization chemistry in the IMS. The bottom two traces illustrate the compounds using an altered chemistry with a charge transfer agent added. Note the peak in each of the

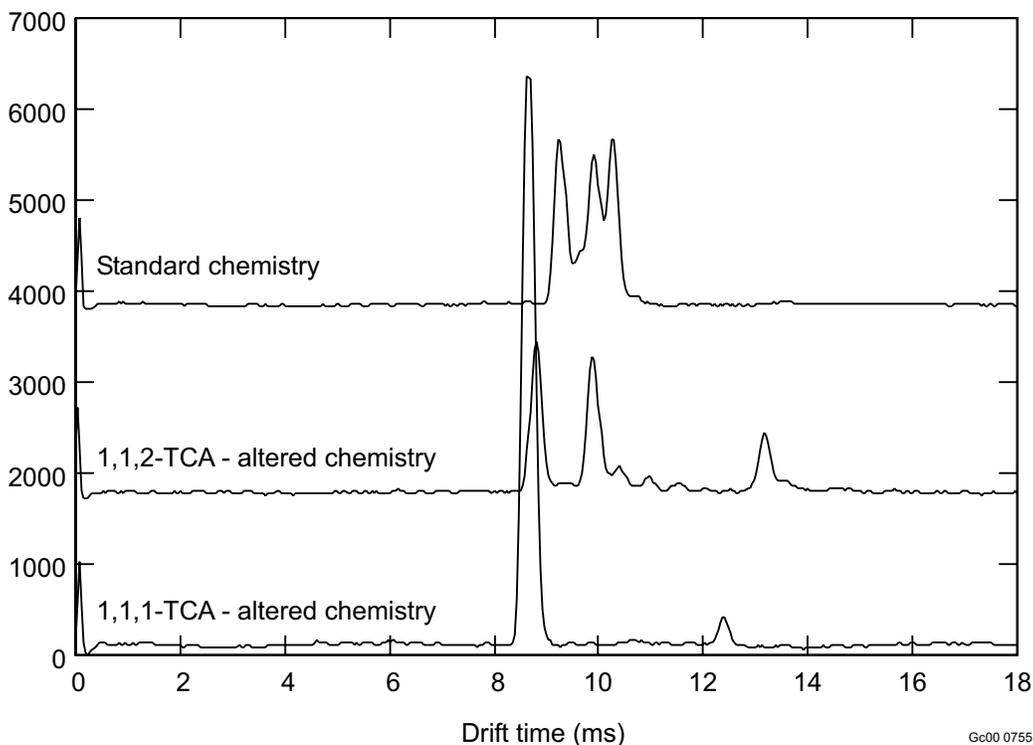


Figure 10. Tetrachlorinated ethanes via differing ionization chemistries.

bottom two traces to the right of 12 ms. This product ion peak is most likely due to a molecular species of the chlorinated hydrocarbons or a cluster. In either case, there is a unique product ion present which can be used to identify the species.

ACCOMPLISHMENTS

This task is successfully applying new technology ideas to long running environmental issues. As the paradigm shift in analytical chemistry takes the traditional laboratory analysis and moves it to real time portable instrumentation used in the field, IMS will be a major player. IMS is a highly sensitive, yet versatile and rugged instrument that will be a focus in environmental monitoring measurements in the field. There are some issues in applying IMS immediately to environmental analysis, such as subsurface deployment and measurement, aqueous sample analysis, and chlorinated solvent contamination response. These issues are being directly addressed and solved by the subtasks in this task.

This task successfully demonstrated how some of the issues of moving IMS into environmental analysis can be overcome. One subtask developed a novel IMS system (FAIMS) for deployment into the subsurface to provide chemical measurements. The system provided quality data on environmentally important analytes during the laboratory testing phase, and will be deployed in the field during the next phase of testing. Part of this deployment will include a downhole measurement test. This deployment will allow for the collection of analytical data that will be of great value in not only characterization, but in the collection of chemical parameters for modeling subsurface contaminant movement.

A second subtask provides a high speed, field deployable method for analyzing ground and surface waters for various analytes, including organic and inorganic cations and anions. Monitoring water can be challenging due to transport and movement. Contaminant pulses can be difficult to track using the traditional sample/laboratory analysis approach. This subtask provides a real-time monitor for water samples, which can also be set up for unattended operation to monitor levels of specific contaminants. It also provides a rugged, easy to use system that has advantages in time and cost over traditional water analyses.

A third subtask demonstrated a pathway to use IMS in the field for monitoring chlorinated hydrocarbon compounds. Although IMS is an attractive instrument for monitoring volatile organic species in a number of media, its use has been hindered by the difficulties in speciating chlorinated hydrocarbons. Nevertheless, this subtask provides a mechanism by which IMS can successfully measure chlorinated organics in real time without the use of GC. It also suggests a potential path where IMS can be used for other problematic analytes.

This task provides real value to DOE and the INEEL by enhancing analytical capabilities required for environmental monitoring and long-term stewardship. The goal of better, faster, and less costly characterization can be realized through the deployment of new technologies suited to the need, and this research offers new solutions to realize this goal.

REFERENCES

1. R. Bradshaw, "Engineering Approaches and Compromises in the Design of Small IMS Spectrometers," *3rd International Workshop on Ion Mobility Spectrometry, Galveston, TX, October 16–19, 1994*; also, C. S. Harden, "Relative Performance Characteristics of Handheld Ion Mobility Spectrometers—The Chemical Agent Monitor and a New Miniaturized Instrument," *5th International Workshop on Ion Mobility Spectrometry, Cambridge, UK, August 1995*.
2. J. Xu, W. B. Whitten, and J. M. Ramsey, "Miniature Ion Mobility Spectrometry," *8th International Workshop on Ion Mobility Spectrometry, Buxton, UK, August 8–12, 1999*.

3. J. I. Baumbach, D. Berger, J. W. Leonhardt, and D. Klockow, "Ion Mobility Sensor in Environmental Analytical Chemistry-Concept and First Result," *Intl. J. Environ. Analy. Chem.* 1993, Vol. 52, p. 189.
4. R. A. Miller, G. A. Eiceman, E. G. Nazarov, "A Micromachined High-Field Asymmetric Waveform-Ion Mobility Spectrometer (FA-IMS)," *Sensor and Actuators B. Chemical*, 2000, in press.
5. A. Buryakov, E. V. Krylov, A. L. Makas, E. G. Nazarov, V. V. Pervukhin, and U. Kh. Rasulev, *Sov. Tech. Phys. Lett* 17(6), June 1991.
6. I. A. Buryakov, E. V. Krylov, E. G. Nazarov, and U. Kh. Rasulev, *Int. J. Mass Spectrometry and Ion Processes*, Vol. 128, 1993, pp. 143–148.
7. B. Carnahan, S. Day, V. Kouznetsov, and A. Tarassov, "Development and Applications of a Transverse Field Compensation Ion Mobility Spectrometer," *5th International Workshop on Ion Mobility Spectrometry, Cambridge, UK, August 6–9, 1995*.
8. B. Carnahan, S. Day, V. Kouznetsov, M. Matyjaszczyk, A. Tarassov, "Field Ion Spectrometry – A New Analytical Technology For Trace Gas Analysis," *Proceedings of the 1996 International Conference on Advances in Instrumentation and Control, ISA '96*.
9. R. W. Purves, R. Guevremont, S. Day, C. W. Pipich, and M. S. Matyjaszczyk, *Review of Scientific Instruments*, Vol. 69, 1998, pp. 4094–4105.
10. R. Guevremont and R. W. Purves, *Review of Scientific Instruments*, Vol. 70, 1999, p. 1370.
11. G. A. Eiceman, S. Sowa, S. Lin, and S. E. Bell, "Ion Mobility Spectrometry for Continuous On-Site Monitoring of Nicotine Vapors in Air During the Manufacture of Transdermal Systems," *Journal of Hazardous Materials* 1995, Vol. 43, pp.13–30.

Molecular Engineering and Genomics for Development of Environmental Biosensors Using Robust Biocatalysts

Exploring the Genetic Potential of Microbes to Detect Hazardous Metals for Cleanup and Stewardship

Frank Roberto and William Apel (INEEL); Mark Young, David Ward (Montana State University); Brent Payton (Washington State University); John Varley (Yellowstone Center for Resources, Yellowstone National Park)

SUMMARY

Biosensors (biologically-based sensors) offer the potential for improved, more cost-effective detection, monitoring, and surveillance of hazardous metals and radionuclide contaminants in the environment and within large-scale processes; however, more stable enzymes are needed to use this science in harsh environments (e.g., radioactive, highly alkaline, high temperature, or nonaqueous environments). Consequently, organisms that live in “extreme” environments (extremophiles) are being studied rather than those that live in ambient conditions. In FY 2000, high-throughput genomic sequencing was directed towards microorganisms that are likely to be useful in solving DOE environmental problems associated with alkaline radioactive wastes. By determining the complete DNA sequence of a halophilic (salt-loving) bacterium (*Halomonas campusalis*; see Figure 1), bioinformatics permits the assessment of the metabolic potential, and thus, the biochemical functions of this organism that could be applied to DOE wastes. Strategies to use specific functions of the bacterium, and approaches to using the intact microbe in harsh environments can be identified from the genetic blueprint for this microorganism.

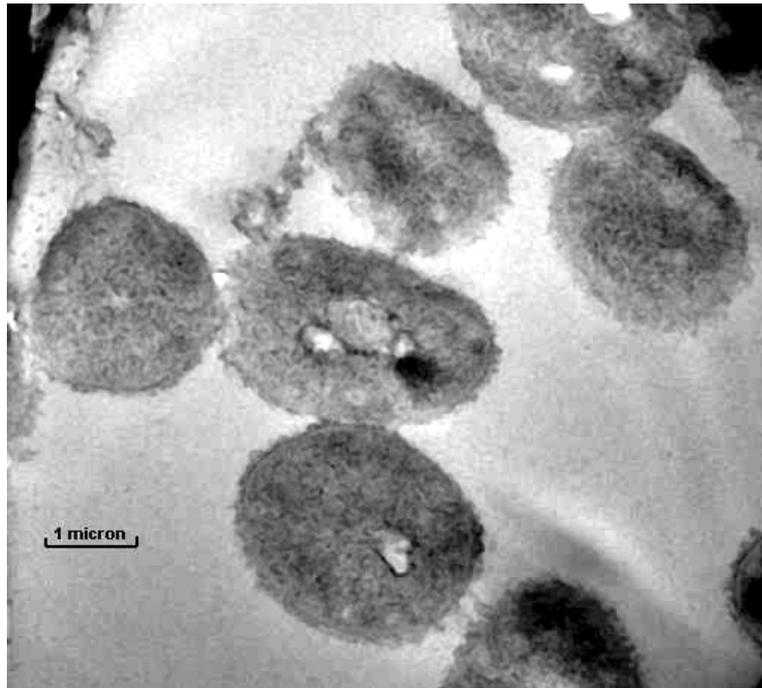


Figure 1. Microscopic photo of the *Halomonas campusalis* bacterium.

The *Halomonas campisalis* organism is of particular interest to this task because of the similarities between its natural environment and the hostile environments found in DOE waste streams, such as the Hanford high level waste tanks. Other research programs at the INEEL investigating radiotolerant bacteria isolated from the Idaho Nuclear Technology and Engineering Center (INTEC) spent nuclear fuel storage ponds may provide an additional target for genomic sequencing. Such an organism would be important from the perspective of survival in high radiation environments.

TASK DESCRIPTION

The objective of this effort is to support the development of biocatalysts that are capable of surviving the harsh physical conditions associated with many environmental processes. These catalysts will have the reaction specificity associated with “conventional” enzymes, but without the inherent instability and related inactivation problems often displayed by enzymes obtained from mesophilic (15 to 37°C circumneutral environmental conditions) organisms. Genomics and molecular biology are crucial to the success of this effort because the DNA sequence of an individual enzyme gene, or a whole extremophilic microorganism, provide access to the genetic blueprint of the individual function or overall metabolic capability. Recently acquired high-throughput sequencing capability in the INEEL is focused on addressing specific functions, and also on the genomic sequencing of a selected halophilic eubacterium (*Halomonas campisalis*). Additional gene and genome targets may be identified in collaboration with our university partners and sequenced, provided funds are available. Because of the intensive nature of genome sequencing, only two, at the most, microbial genomes are contemplated over the course of this task.

The technical approach for genome sequencing uses the following general strategy:

1. Genomic DNA isolated from each candidate is physically sheared to generate fragments in the 2 to 10 kilobase (kb) range; these fragments are enriched by density gradient centrifugation or size fractionation on agarose gels.
2. Fragment size cuts of 2 to 3 kb and 6 to 10 kb are cloned into the vector pCR4Blunt or pUC18, and the resulting libraries are stored as glycerol stocks at -70°C .
3. Libraries are plated and individual colonies picked to deep-well microliter plates for plasmid isolation and purification. Robotics will be implemented in FY 2001 (assuming general purpose capital equipment funds are available) to reduce labor costs associated with this task.
4. Plasmids are screened on 1% agarose gels as a quality check prior to sequencing using Applied Biosystem’s BigDye Terminator chemistry. Sequencing reaction chemistry will also be automated in FY 2001.
5. Sequences are determined on an applied biosystems Model 3700 DNA analyzer and resulting data is assembled into contiguous segments (contigs) after quality assessment and editing.
6. Gene analysis is initiated by BLAST analysis via the National Center for Biotechnology Information (NCBI) servers. In order to streamline this process, network upgrades were performed at the INEEL Research Center (IRC) to provide 100 Mb/s bandwidth for data obtained in the laboratory. Workstation upgrades are currently underway to improve throughput of raw sequence information through automated sequence editors and alignment algorithms. The INEEL Visualization Group is also providing technical support and accounts on Sun Enterprise servers to accelerate the bioinformatics activities of this task.

Halomonas Campisalis

Halomonas campisalis is a member of the Family *Halomonadaceae* and is part of the gamma subdivision of the Proteobacteria.¹ Based on 16S rRNA sequence analysis, the organism was placed in this family because of a distinctive cytosine residue at position 486, which is found in all members of the *Halomonadaceae*, including *Deleya*, *Volcaniella*, and *Chromohalobacter*.² *Halomonas campisalis* was isolated from Alkali Lake in Washington and characterized as a new species because of DNA-DNA hybridization experiments as well as phenotypic and phylogenetic studies with other members of the *Halomonas* genus.³ Although it can tolerate a wide range of salt, pH, and temperature, it grows optimally in 1.5M NaCl, pH 9.5, and 30°C.⁴

DOE-SC has supported the genomic sequencing of such an organism, *Deinococcus radiodurans*, through the Microbial Genome Program.⁵

Library Construction and Sequencing

Isolation of genomic DNA was found to be efficient using conventional techniques. Purified DNA was sheared by passage through a nebulizer to produce fragments ranging from 1 to 4 kilobases (kb) in size, and cloned into the plasmid vector, pCR4Blunt-TOPO (Invitrogen, La Jolla, CA) per manufacturer's recommendations. Resulting clones were purified using 96-well plasmid isolation kits (PerfectPrep-96Vac, Eppendorf, Boulder, CO). Purified plasmid DNA was quantified by ultraviolet absorbance measurement at 260 nm, or by comparison with known quantities of DNA after agarose gel electrophoresis. Sequencing reactions were performed using fluorescent dideoxynucleotide analogs (BigDye Terminator Ver. 2.0, Applied Biosystems, Foster City, CA) and sequences determined on a Model 3700 DNA analyzer (Applied Biosystems, Foster City, CA). To date, over 600 sequences have been generated.

Bioinformatics

Preliminary analysis is being performed by manual submission of sequences to the servers at the NCBI basic local alignment search tool (BLAST). Any identifications returned require manual evaluation prior to gene assignments. Table 1 lists some of the best "hits" so far.

ACCOMPLISHMENTS

Our accomplishments during FY 2000 are as follows:

- Established a high-throughput genomics capability at the INEEL (instrumentation purchased with INEEL general purpose capital equipment funds)
- Constructed genomic libraries to provide a source of small DNA fragments for sequencing of *halomonas campisalis*, a halophilic (salt-loving) bacterium
- Upgraded laboratory network and computational infrastructure for bioinformatics
- Generated and analyzed genomic sequence information from *halomonas campisalis*.

Table 1. BLAST gene identifications (using blastx) for *Halomonas campisalis* library clones.

Plate ID	Description
A10 92600	<i>Sphingomonas aromaticivorans</i> putative aromatic efflux pump membrane protein
E07 91900	<i>Bacillus halodurans</i> phage-related protein
F02 92600	<i>Bacillus halodurans</i> flagellar biosynthesis (<i>flhS</i>)
F03 91900	Acriflavin resistance protein
F06 92600	Phosphate acetyltransferase
G02 91900	Sulfonamide resistance protein
G05 91900	Phosphoenolpyruvate carboxylase
G06 91900	Terminal dioxygenase
G07 91900	AcoR transcriptional regulator
G07 92600	Serine-threonine kinase
H02 91900	DNA polymerase III
H11 92600	TonB-dependent receptor
A11 92600	Cation transport ATPase
B06 92600	Phosphate ABC transporter
B08 91900	Putative GlcNAc transferase
C08 91900	Conserved hypothetical protein
D02 91900	Putative ATP-dependent helicase
D05 91900	<i>Bacillus halodurans</i> transposase

REFERENCES

1. A. Balows, H. G. Truper, M. Dworkin, W. Harder, and K. H. Schleifer, *The Prokaryotes*, (ed.) 1992, 2nd ed., Volume IV, Springer-Verlag, New York.
2. E. Mellado, E. R. B. Moore, J. J. Nieto, and A. Ventosa, "Phylogenetic Inferences and Taxonomic Consequences of 16S Ribosomal DNA Sequence Comparison of *Chromohalobacter marismortui*, *Volcaniella eurihalina*, and *Deleya salina* and reclassification of *Volcaniella eurihalina* as *Halomonas eurihalina* comb," *Int. J. System. Bacteriol*, 45, November 1995, pp. 712-716.
3. M. R. Mormile, M. F. Romine, M. T. Garcia, A. Ventosa, T. J. Bailey, and B. Peyton, "*Halomonas campisalis* a Denitrifying, Moderately Haloalkaliphilic Bacterium," *System Appl. Microbiology*, 22, sp. November 1999, pp. 551–558.
4. F. Ausubel, R. Brent, R. E. Kingston, D. D. Moore, J. G. Seidman, J. A. Smith, and K. Struhl, *Short Protocols in Microbiology*, (ed.) 1999, 4th Edition, John Wiley and Sons, New York.
5. O. White, J. A. Eisen, J. F. Heidelberg, E. K. Hickey, D. Peterson, R. J. Dodson, D. H. Haft, M. L. Gwinn, W. C. Nelson, D. L. Richardson, K. S. Moffat, H. Qin, L. Jiang, W. Pamphile, M. Crosby, M. Shen, J. J. Vamathevan, P. Lam, L. McDonald, T. Utterback, C. Zalewski, K. S. Makarova, L. Aravind, M. J. Daly, C. M. Fraser, et al., "Genome Sequence of the Radioresistant Bacterium *Deinococcus Radiodurans*R1," *Science* 286 (5444), 1999, pp. 1571–1577.

Biologically Based Catalysts as Sensors to Detect Contaminants in Harsh Service Environments

Harnessing Microbial Enzymes to Detect Hazardous Metals for Cleanup and Stewardship

William Apel and Vicki Thompson

SUMMARY

Harnessing and controlling the effects of microbial activity is of significant interest to DOE in their environmental cleanup and long-term stewardship mission. Microbes called extremophiles exist that thrive in even the harshest of environments, and which offer promise as biologically based sensors.

This research focuses on developing catalysts—substances that control the rate of chemical reactions—that are effective in the harsh conditions associated with many existing industrial and environmental processes. These catalysts will ultimately form the basis of new real-time biologically based sensors for detecting hazardous metals and radionuclides in the environment. Our initial effort concentrates on developing enzymes from extremophiles, since these microorganisms literally live at life's physical extremes, such as very high or low temperatures, or high radiation fields. Extremozymes derived from these microorganisms often share their adaptation to extreme conditions and maintain their specific catalytic activity and stability under the same extreme conditions.

We are currently analyzing enzymes for various properties to learn how to optimally use the enzymes in a sensor, and will develop and test first-generation sensors for stability under varying temperature and pH conditions.

TASK DESCRIPTION

Background

Heavy metal contamination is a pervasive problem throughout the DOE complex and the United States. A recent report shows lead, chromium, arsenic, zinc, copper, cadmium, nickel, and mercury contamination in soils and groundwater at 16 DOE sites.¹ Similar metals have been found at approximately 75% of Superfund sites across the United States.²

Current methods to assess and monitor sites for heavy metal contamination include atomic absorption and inductively coupled plasma emission spectrometry. These methods, while sensitive and reliable, are not readily adapted to field use. Samples must be sent to a remote laboratory for analysis, and results are often delayed for weeks, making these methods unsuitable for continuous monitoring of contaminated sites. Additionally, analysis using these methods is expensive, and thorough characterization of contaminated sites is often economically unfeasible. Owing to these drawbacks, new methods are required for inexpensive, continuous, and high sensitivity, high reliability monitoring of contaminated sites. Biological sensors offer a solution. Biological sensors consist of two parts: a biological part, such as antibodies, enzymes or whole cells; and a transducer, such as optical fiber, a field effect transistor, or an amperometric sensor.³ The compound to be measured reacts with or binds to the biological part of the sensor and generates a signal based on the strength of this interaction. Signals that can be generated include production of fluorescent or luminescent compounds, generation or consumption of electrons, and generation of heat. The transducer picks up the signal and generates an output, such as a current or voltage. Because

biological reactions are highly specific for their target compound, sensors can be produced with sensitivity in the part-per-billion or part-per-trillion range. This specificity also gives biosensors the advantage for measuring complex mixtures, and reduces or eliminates the necessity of removing interfering compounds in samples prior to measurement. Finally, biological reactions are rapid. Typically, measurement with biological sensors can be performed in a few minutes. Despite these advantages, biological sensors have one serious drawback: fragility of the biological component to extreme conditions. Most biological systems (mesophiles) are active within only a narrow range of conditions, typically 20 to 40°C, near neutral pH, and low salt concentrations. Outside this range, the activity and stability of biological systems fall off rapidly, which limits their use in biosensors to the same narrow range of conditions. Our solution to this problem is to use biological components derived from extremophilic microorganisms. These organisms thrive under extremes of temperature (up to 110°C and below 20°C), pH (below 4 and above 9), salt concentration (up to 5M), or pressure (up to 500 atm).⁴ Biological components such as enzymes derived from these organisms typically share their tolerance for extreme conditions. Use of these types of enzymes would produce a biological sensor capable of measurement under extreme conditions, and would be more stable than enzymes derived from mesophilic organisms.

A number of biosensors have been developed for detecting heavy metals. These sensors rely on the inhibition of many enzymatic reactions in the presence of heavy metals. Classes of enzymes that have shown this behavior include ureases, peroxidases, phosphatases, cholinesterases, dehydrogenases, reductases, and oxidases.⁵ As an example, a metal ion biosensor was developed using the enzyme lactate dehydrogenase that had a limit of detection of 0.4 ppb for mercury. The sensor can also detect other metals, including silver, lead, copper, and zinc.⁶

For this ESRC task, we plan to isolate and purify two enzymes: one derived from a thermophilic organism (catalase), the other from a halophilic organism (nitrate reductase). This will be done during the latter half of FY 2000 and the first half of FY 2001. Additional funding will be pursued to characterize enzyme kinetics, stability, tolerance to extreme conditions, and inhibition by heavy metals. After characterization, we will use the enzymes to develop heavy metal biosensors that will be characterized for sensitivity and selectivity and then field tested at contaminated sites.

Task Summary: Catalase

The enzyme catalase catalyzes the dismutation reaction of hydrogen peroxide to form water and oxygen, as $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$.

The enzyme is found in most aerobic organisms and protects cells against oxidative damage caused by hydrogen peroxide. The average molecular weight of catalases is 240,000 and typically consists of four to six identical subunits that all have catalytic activity. Catalases are usually heme enzymes, though Mn catalases have also been reported. Reports from the literature indicate that catalases are sensitive to several heavy metals, including Cu, Fe, Pb, Zn, and Ni.⁷

Thermophilic microorganisms (49 strains) isolated previously from Yellowstone National Park hot springs and from Amalgamated Sugar (Twin Falls, Idaho) process streams were tested for catalase activity, and 28 of those strains tested positive. We selected the strain showing the strongest catalase reaction for isolation of the catalase enzyme. This strain was identified through 16S RNA analysis as *Thermus brockianus*.

This isolate was grown aerobically at 70°C in 4-liter cultures to obtain sufficient biomass to isolate the enzyme. We examined several methods for cell lysis, including chemical treatment, sonication, and the French press. The best results were obtained using the French press. After the cells had been lysed, we removed cell debris by centrifugation and kept the supernatant for further purification. After examining

the catalase literature, we developed a purification strategy that included the following steps: precipitation, ion exchange chromatography, hydrophobic interaction chromatography, and gel filtration chromatography.

We first examined precipitation of the enzymes through the salting out effect. Sequential additions of ammonium sulfate were added to the crude cell extract to precipitate proteins. After each addition, we centrifuged the solution to remove precipitated protein and kept the pellet for further analysis. Ammonium sulfate concentrations of 20, 40, 60, and 80% of saturation were used in this study. Each pellet was resolubilized in buffer and tested for catalase activity. The catalase activity was distributed fairly evenly through all the ammonium sulfate cuts, and no one cut represented the bulk of the enzyme activity. Since this step did not result in appreciable purification, we did not pursue it further.

Next, we investigated ion exchange chromatography as the first purification step. This technique separates proteins based on their net charge. We selected a diethylaminoethyl (DEAE) anion exchange column for this application. Crude cell extract was loaded onto a DEAE column and washed with buffer. Proteins were eluted off the column with increasing amounts of salt (0 to 1.0 M KCl) in a stepwise fashion. Figure 1 shows the results from a typical run. A large amount of protein did not bind to the column and passed through during the wash step, but had very little catalase activity. As we increased the salt concentration to 0.25 M, we saw a second peak with high catalase activity. The last peak came off at 0.5 M KCl, and, again, there was very little catalase activity present. Further increases in salt concentration did not release any more protein. We optimized ionic strength and pH by examining column performance at pH ranging from 4 to 9 and buffers from 10 to 100 mM. Optimum conditions were found at 20-mM buffer strength and pH of 8.0.

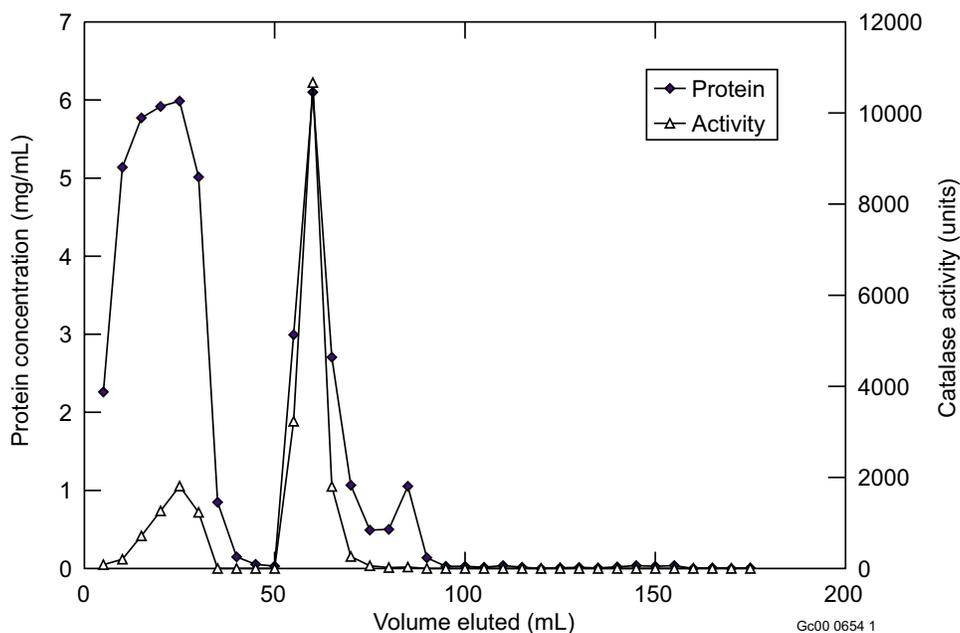


Figure 1. Results of DEAE ion exchange chromatography.

The high catalase activity fractions obtained from the DEAE column were pooled, brought up to 1.0-M ammonium sulfate, and applied to a hydrophobic interaction column that separated the proteins based on their hydrophobicity. Reducing the salt concentration in a stepwise fashion caused the proteins to become less hydrophobic, and they were eluted from the column (see Figure 2). Each decrease in salt

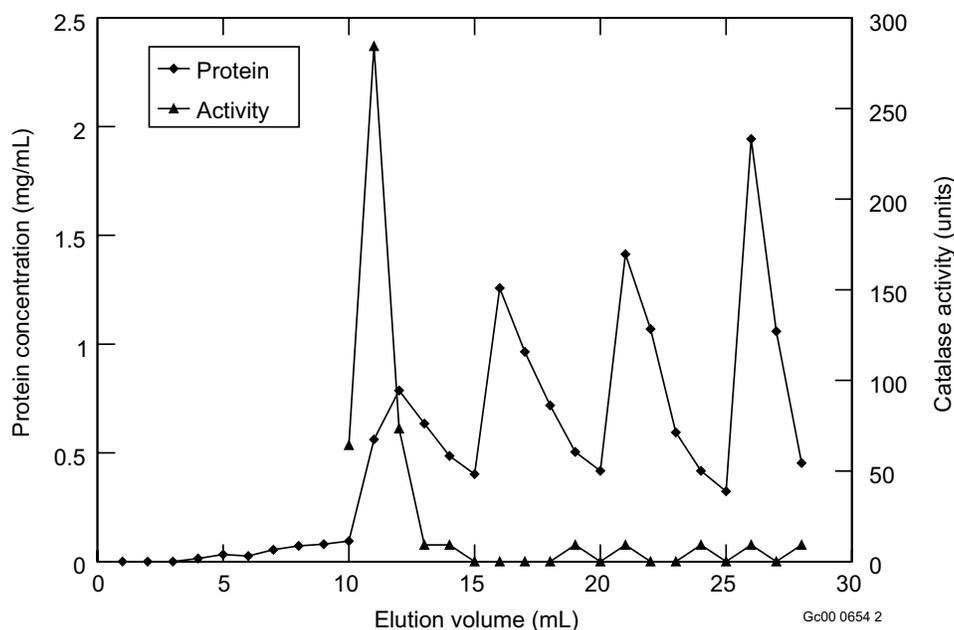


Figure 2. Results from hydrophobic interaction chromatography (HIC).

concentration resulted in a protein peak from the column. The bulk of the catalase activity came off in the first peak. We examined five different types of hydrophobic interaction columns and found the phenyl active group gave best results.

Table 1 summarizes the purification obtained from each step. The ion exchange chromatography step resulted in a small amount of purification, as evidenced by the increase in specific activity (units of activity divided by total protein present); however, the hydrophobic interaction chromatography resulted in the most purification. The 30% yield is typical of protein purification protocols seen in the literature. We also subjected the proteins to gel electrophoresis to see how much contaminating protein was present after each step (see Figure 3). After each chromatography step, the number of bands present decreased, indicating that contaminating proteins had been removed. At least one more purification step will be necessary to remove all the contaminating protein. We will examine gel filtration as the next step.

This task will continue into FY 2001 with the ultimate goal to complete purification of the catalase enzyme. This will entail optimizing the hydrophobic interaction chromatography step and optimizing the gel filtration chromatography. Additionally, milligram quantities of the enzyme will be produced after the purification procedure has been fully developed. Future work (not part of the ESRC task) will center on characterizing enzyme properties and its inhibition by metal ions, and developing and testing a catalase metal ion biosensor.

Table 1. Summary of protein purification.

	Total Units (U)	Specific Activity (U/mg)	Purification (fold)	Yield (%)
Cell extract	1420	87	1	100
DEAE step	1100	118	1.3	77
HIC step	420	5390	62	30

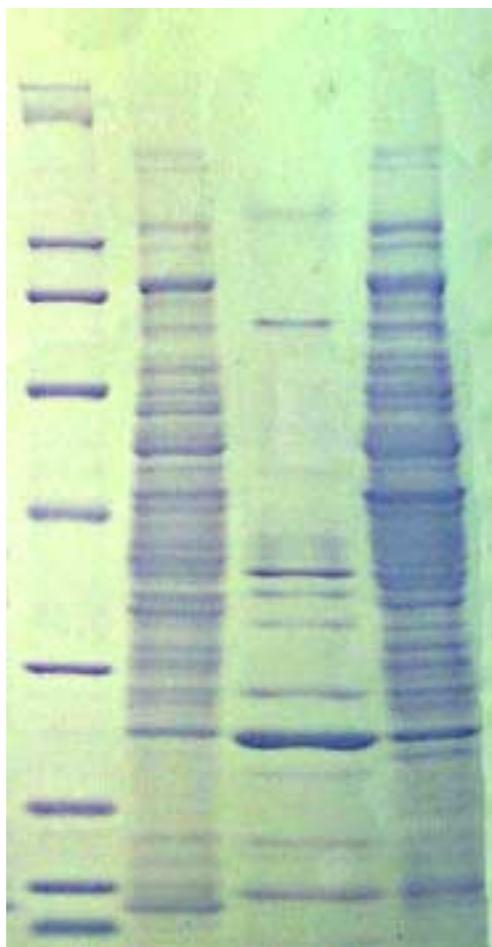


Figure 3. Gel electrophoresis of each stage of purification. Lane 1—molecular weight standards, Lane 2—DEAE fraction, Lane 3—HIC fraction, and Lane 4—cell extract.

Task Summary: Nitrate Reductase

Nitrate reductase catalyzes the reduction of nitrate to nitrite. This enzyme is typically about 230,000 molecular weight and consists of three subunits. In contrast to catalase, each subunit is a different size and serves a different function. Previous work shows that nitrate reductase is sensitive to chromium, lead, nickel (see Figure 4), copper, zinc, and cadmium.⁸

This task is being conducted at Washington State University by a graduate student (Abbie Aiken) under the guidance of Drs. James Peterson and Brent Peyton and focuses on purifying nitrate reductase from a halophilic microorganism, *Halomonas campisalis*.⁹ Additionally, further research was conducted characterizing the inhibition of nitrate reductase by metals in the presence of chelators.

The growth curve for *Halomonas campisalis* was determined in batch cultures (see Figure 5). After a short lag phase, this organism had a 12-hour log growth phase followed by entry into a stationary phase at 16 hours of growth. We also conducted a study to determine the amount of nitrate reductase produced during each phase of growth and to find the optimal time to harvest the culture. The relative amount of nitrate reductase increased with increased biomass and leveled off as the stationary phase was reached. These results indicate that the optimal time to harvest cells is during the late log or early stationary phase.

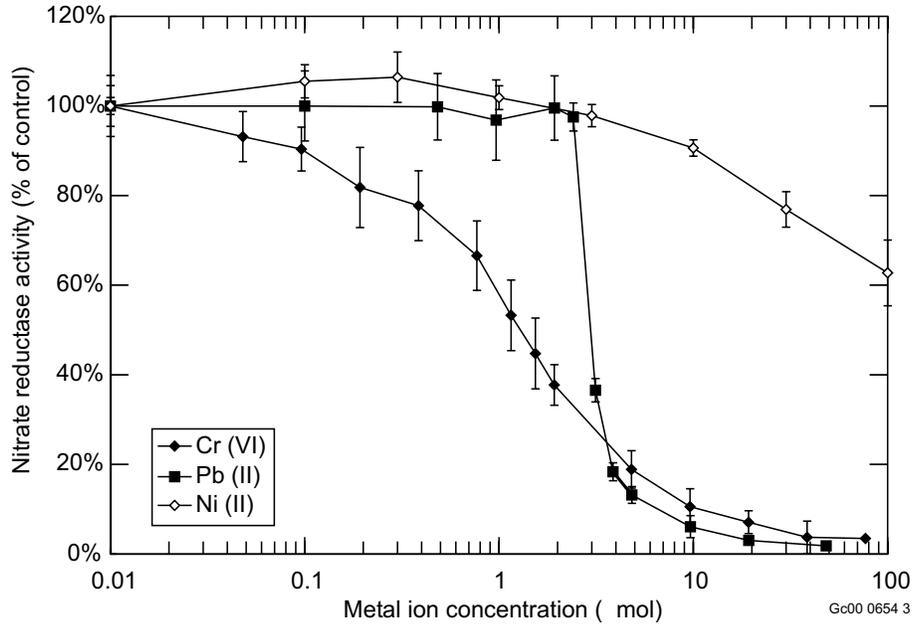


Figure 4. Inhibition of nitrate reductase by various heavy metal ions.

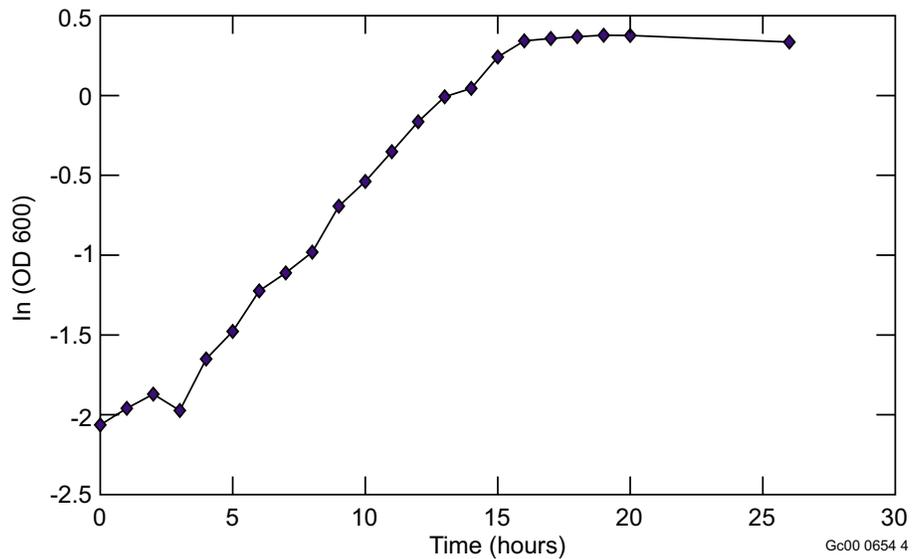


Figure 5. Growth curve for *Halomonas campisalis*.

We searched the literature to examine purification strategies for nitrate reductase and developed the following strategy for purifying nitrate reductase from *Halomonas campisalis*.¹⁰ We will lyse cells with a French press and centrifuge to remove cell debris. Since nitrate reductase is a membrane bound enzyme, we will subject the supernatant to ultracentrifugation (70,000 g) to separate cell membranes from the soluble protein fraction. The pellet will be resolubilized, nitrate reductase will be separated from the membranes with a detergent, and the solution centrifuged again at 70,000 g. We will then subject the supernatant to ion exchange chromatography, hydrophobic interaction chromatography, and gel filtration chromatography. Buffer concentrations, pH, and ionic strengths will be optimized for each chromatography step.

Finally, we examined the inhibition of nitrate reductase caused by various metals in the presence of a metal ion chelator, EDTA (ethylenediaminetetraacetic acid) (see Figure 6). Zinc was completely non-inhibitory to nitrate reductase in the presence of even low levels of EDTA, indicating that the EDTA completely chelated the zinc. Chromium (VI), on the other hand, still inhibited nitrate reductase with up to 100 mM EDTA present. These results show it is possible to completely remove the inhibition of a given metal by adding metal ion chelators. This is an important result for future metal ion biosensor development, since it will be possible to make a biosensor that is specific for a given metal, simply by adding different metal ion chelators.

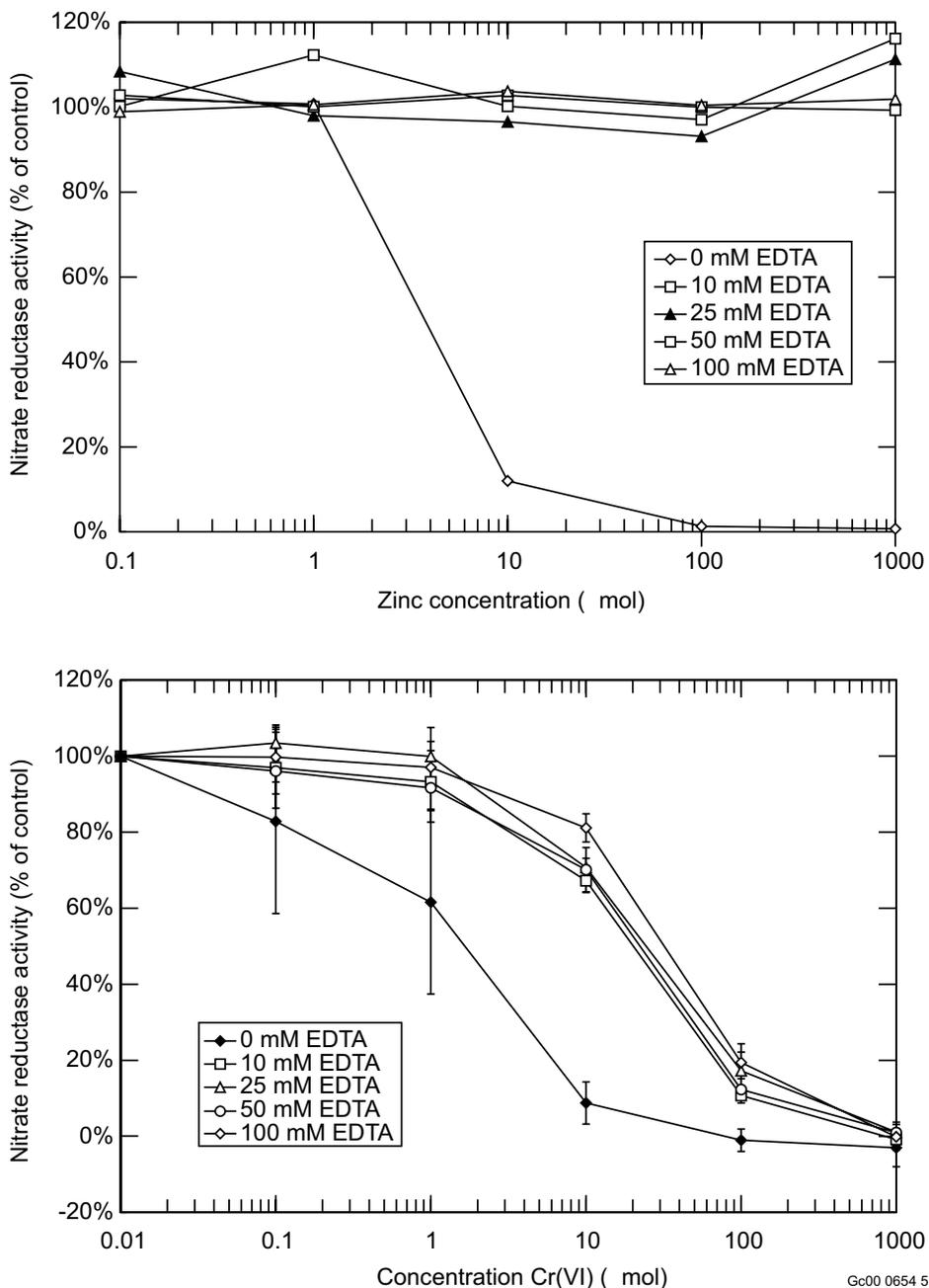


Figure 6. Metal inhibition of nitrate reductase in the presence of metal ion chelator, EDTA. a) Zn; b) Cr(VI).

This task will also continue into FY 2001, and the goal will be to complete purification of nitrate reductase from *Halomonas campisalis*. Future work (not part of the ESRC task) will entail characterizing the nitrate reductase enzyme and developing a metal ion assay with the enzyme.

ACCOMPLISHMENTS

Our accomplishments during FY 2000 are as follows:

- Discovered a thermophilic organism with catalase activity
- Identified that thermophilic organism through 16S RNA as *Thermus brockianus*
- Developed a purification strategy for catalase
- Optimized ion exchange chromatography
- Initially developed a hydrophobic interaction chromatography step
- Achieved 60-fold purification of catalase through two purification steps
- Characterized the *Halomonas campisalis* strain, to be used for purifying nitrate reductase
- Assessed metal inhibition characteristics of nitrate reductase
- Developed a purification strategy for nitrate reductase through studying the literature
- Started optimization of ion exchange chromatography step for nitrate reductase.

REFERENCES

1. R. G. Riley, and J. M. Zachara, *DOE/ER-0547T*, 1992.
2. C. R. Evanko, and D. A. Dzombak, "Technology Evaluation Report TE-97-01," Pittsburgh, PA: GWRTAC, 1997.
3. M. A. Arnold, and M. E. Meyerhoff, "Recent advances in the development and applications of biosensing probes," *CRC Critical Reviews Anal. Chem.*, Vol. 20, No. 3, 1988, pp. 149–196.
4. M. W. W. Adams, and R. M. Kelly, "Enzymes from microorganisms in extreme environments," *Chemical & Eng. News*, Dec. 18, 1995.
5. T. K. Krawczyk, "Analytical applications of inhibition of enzymatic reactions," *Chem. Anal. (Warsaw)*, Vol. 43, 1998, pp. 135–157.
6. S. Fennouh, V. Casimiri, A. Geloso-Meyer, and C. Burstein, "Kinetic study of heavy metal salt effects on the activity of L-lactate dehydrogenase in solution or immobilized on an oxygen electrode," *Biosensors & Bioelectronics*, Vol. 13, 1998, pp. 903–909.
7. M. P. Popova, and C. H. S. Popov, "Effect of heavy metal salts on the activity of rat liver and kidney catalase and lysosomal hydrolases," *J. Vet. Med. A*, Vol. 45, 1998, pp. 343–351.

8. A. Aiken, B. Peyton, J. Peterson, and W. Apel, "Metal-induced inhibition of nitrate reductase," *Second Internat. Biometals. Symp, Tübingen, Germany, 2000*.
9. M. R. Mormile, M. F. Romine, M. T. Garcia, A. Ventosa, T. J. Bailey, and B. M. Peyton, "*Halomonas campisalis* sp. nov., a denitrifying, moderately haloalkaliphilic bacterium," *Sys. Appl. Microbiol.*, Vol. 22, 1999, pp. 551–558.
10. K. Yoshimatsu, Sakurai, and T. Fujiwara, *FEBS Letters*, Vol. 470, 2000, pp. 216–220.

Determining Soil Moisture Over Wide Areas for DOE Site Stewardship Hydrology

Wide-Area Moisture Sensing and Mapping

John (Jack) M. Slater, John M. Svoboda, and James Lee

SUMMARY

This goal of this research task is to develop a new sensing technology to detect subsurface moisture in soils. Knowing the subsurface moisture in soil over wide land areas is valuable information for hydrological studies (as a boundary condition), land-fill cover assessments, monitoring of DOE stewardship lands, and monitoring of exposed contaminated wastes where water flux must be monitored.

Thus far, we have developed a platform for sensors that can be embedded in soil (or elsewhere) and communicate by novel short-range telemetry. The technology will facilitate low-cost acquisition of data for hydrological studies and for long-term monitoring relating to environmental stewardship. The key characteristic of the technology is that the buried sensors are passive, i.e., they have no internal power; they communicate with a reader by short-range inductive magnetic coupling. Accordingly, the sensor will have a long lifetime and require no maintenance. Nearly all our efforts have gone into developing the platform rather than any specific sensor. Our initial demonstration was to sense moisture.

The passive telemetry architecture has general utility when sensing is required without physical connection between the probe and reader, and when the probe must operate over extended time. This sensing technology can be used to sense chemical species within a sealed container, moisture below a moisture cap in a landfill, and chemical process parameters such as acidity, with a probe travelling in a process stream (which could be within a living organism).

The key component of the technology is a long-lived, passive probe that can be embedded in any nonconductive media at desired measurement points. The probe carries passive telemetry for communication with a data logger. Electrical power for the telemetry is derived from magnetic induction between the probe and a small inductive loop within the reader. The probe contains a sensor (moisture or other) that is also driven from this power. We estimate that the physical separation between the probe and reader is viable to at least two meters, using the approach described herein. If the probe carries a moisture sensor based on measuring the soil dielectric constant, the outer surface of the probe can be fully inert (e.g., plastic), so life expectancy is long. Accelerated aging tests for integrated circuits often predict failure rates that exceed 100 years, even for continuous operation at 55°C ambient temperature.¹ Failure rates at low temperatures can be substantially lower.

We call this sensor platform architecture the passive telemetered probe (PTP), which contains the sensor (or sensors), the telemetry unit, and the remote reader. This architecture was designed with long-term monitoring of landfill caps in mind, but the concept is widely applicable.

Monitoring the performance of landfill barriers can determine when a barrier is operating within previously determined limits, or to calculate performance parameters such as water flux through the landfill cap. Little research has been conducted to establish viable strategies for long-term monitoring. Often, life-cycle monitoring costs at closed waste sites are estimated to 30 years without consideration of additional monitoring. At present, a water moisture monitoring strategy might involve multiple embedded sensors, each wired to a data logger or telemetry unit. The wires present obstacles to heavy equipment at

the time of cap construction and subsequent cap maintenance, and use of wired sensors also implies cap penetrations. Any maintenance of sensors means additional penetrations. Our goal is to offer a penetration-free, maintenance-free monitoring system.

The general configuration as it relates to a landfill cap can be understood from Figure 1. The basic approach is that one or more probes, in this case probes containing moisture sensors and passive telemetry, are mounted at points of interest that will allow determining the integrity of the landfill cap.

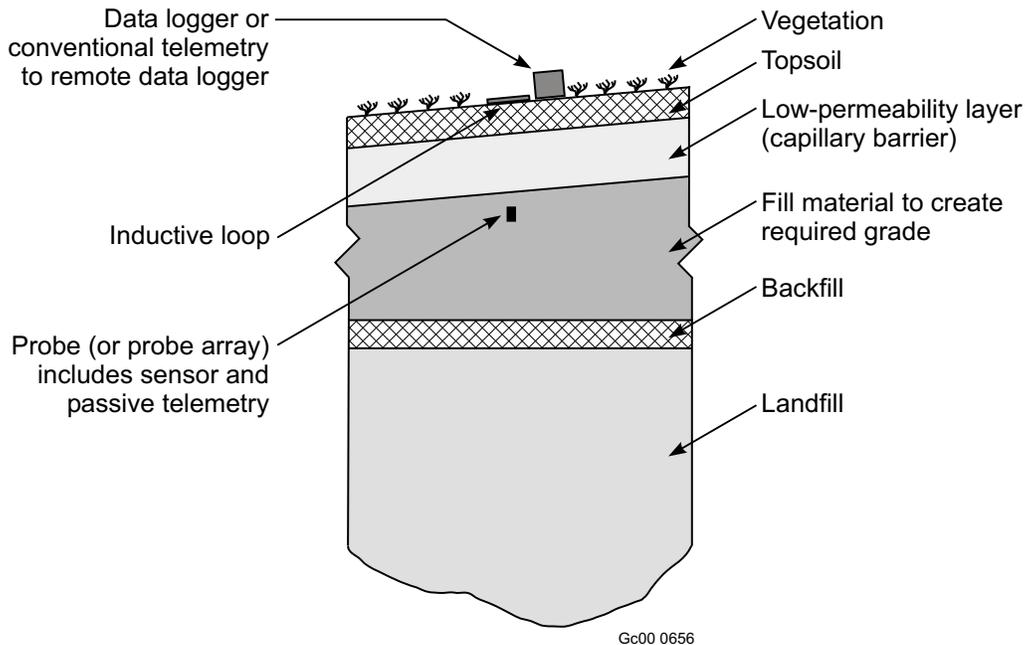


Figure 1. Cross-section showing a landfill barrier.

We recognize that the cap must retard the downward flow of moisture, e.g., by an actual barrier or by evapotranspiration from vegetation. At least one probe would be mounted below the cap's moisture barrier, while the inductive loop of the reader, which requires power, resides on top of the barrier. The moisture barrier within a landfill cap generally does not exceed two meters in depth, even for complex designs.² The data logger can be located at any convenient spot, and linked by conventional radio frequency telemetry to the reader. Use of multiple probes with a single reader is possible, allowing measurement of vertical moisture profiles and area monitoring. Moisture infiltration maps can be generated from such data.

This sensor architecture has several desirable attributes: (a) there are no wires to impede barrier construction activity; (b) there is no penetration of the barrier; (c) the probe can be robust and small, and thereby useful as an insertion-mounted retrofit to existing caps; (d) data acquisition can be remote and automated, as long as it is consistent with the approximate two-meter limitation between probe and reader; (e) the probe is low-cost and deployable in large numbers; (f) multiple sensors can be incorporated into a single probe; and (g) multiple probes can be interrogated by a single reader.

The overall status of the research is that we have performed an end-to-end system demonstration of the PTP using an existing time domain reflectometry (TDR) moisture sensor. All work was at the breadboard level and over only a short range between the probe and reader, about 60 cm. We expect that that range will be increased substantially as the system is optimized. The anticipated range after development is about two meters. Our work constitutes proof-of-principle demonstration.

TASK DESCRIPTION

The telemetry concept is for low-frequency magnetic fields, approximately 125 kHz, to carry both energy and information. Low frequency has acceptable penetration in moist soil. Key parameters relating to penetration depth are the soil electrical conductivity and the frequency of the penetrating field. The magnetic field is attenuated roughly at the same rate an electromagnetic field would be, the latter being governed by the well know skin depth equation. Conductivities in arid soils have been measured at the INEEL³ with typical maximum (saturated soil) direct current values of order 0.1 siemen/meter. Using this value, we expect that attenuation is not important if we stay with low frequencies and distances of about two meters or less. For reference, the electromagnetic skin depth at 100 kHz and the above conductivity value is 5 m. Von Hippel⁴ has measured conductivity values at 100 kHz, but for lower moisture levels, which is consistent with this 5-m estimate.

The system is designed around a microcontroller produced by Microchip Technology.^a It is essentially a single-chip computer programmable in a C-like language. It contains onboard nonvolatile memory, multiple analogue-to-digital (A/D) channels, and digital communication ports. The microcontroller can handle all the logic needed for power management, operation of a sensor, and communication with the reader.

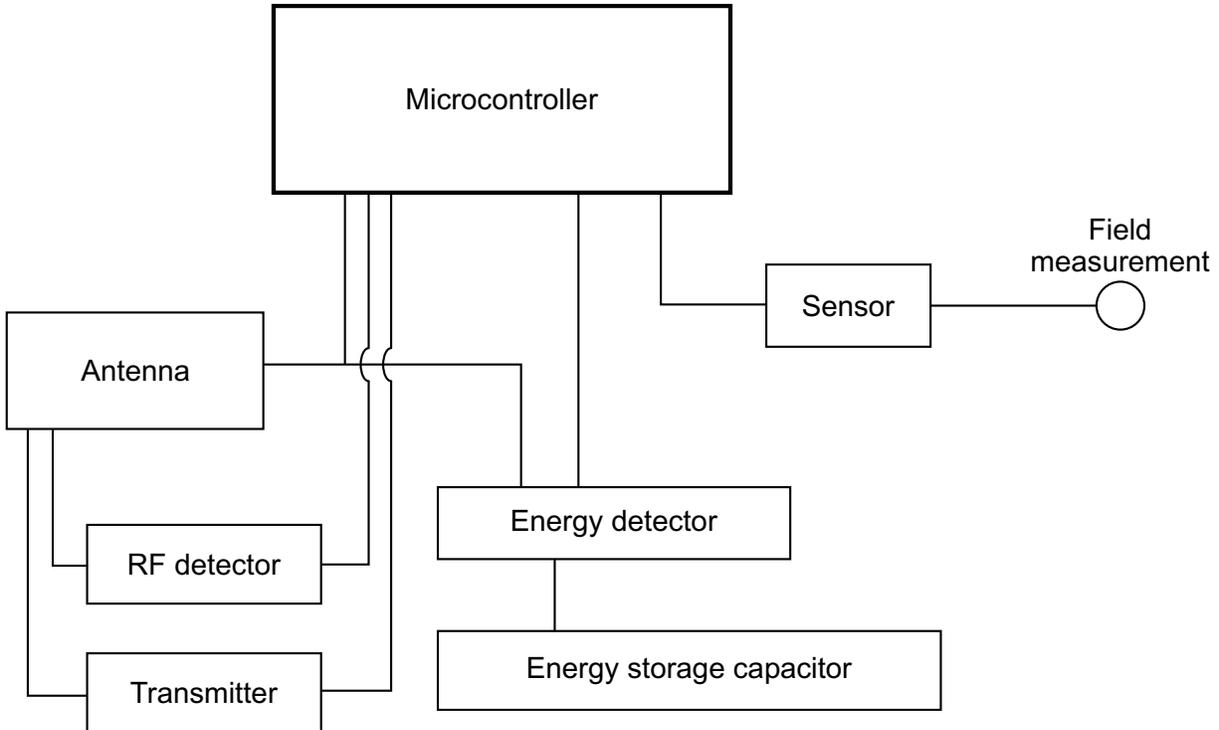
For the reader to acquire a reading from the probe, the basic sequence is as follows. The reader first sends out energy in the form of a pulsating magnetic field, which is captured and stored in a capacitor within the probe. The captured energy then powers the microcontroller, which instructs the sensor to perform a measurement. This value (e.g., moisture content) is then digitized. At that point, the microcontroller powers the probe transmitter and also controls frequency-shift keying to impress the digital reading on the transmitted waveform, with subsequent decoding by the reader. A variation would be that the reader supplies instructions to the probe, as well as energy. For example, the probe might be instructed to report the value of a particular onboard sensor or to adjust the operating range of a sensor.

Figure 2 shows a simplified block diagram of the probe. The antenna, actually a resonant circuit, is used both for capturing energy from the reader and transmitting data back to the reader. As energy builds in the storage capacitor, the microcontroller begins to operate and polls the energy detector circuit to determine if the capacitor is fully charged, in which case about 5 volts are available. When that condition is achieved, the RF detection circuit is polled to determine if the reader (not shown) is still transmitting the energizing pulse. If not, the reader has stopped to listen. If so, the microcontroller interrogates the sensor, which requires applying power to it and digitizing its analog output.

At this point, the measurement result is stored in the microcontroller's memory. Power is then applied to the transmitter, which in turn drives the antenna. Frequency-shift keying is accomplished by switching a small capacitance in and out of the resonant circuit of the antenna; the switching is controlled by the communications port on the microcontroller.

The receiving process is straightforward. An FM receiver is tuned such that its passband is centered on one of the frequency components of the modulated wave. This produces analogue output from the receiver that is level shifted to become a proper RS-232 signal. That signal is captured by the serial port of a computer, which serves as the data logger.

a. Programmable Interface Controller PIC16F876-04/SP produced by Microchip Technology, Inc. A low-power version of this chip is available (but not used in this program), PIC16LF876-04/SP. The differences are indicated in Table 1.



Gc00 0657

Figure 2. Simplified block diagram of the probe.

One of the most important elements of the whole system is the method of power management within the probe, since the probe must operate on the low power available from the induced currents. Table 1 presents the basic power management information. The charge rate refers to current delivered to the probe's energy storage capacitor. The given value corresponds to use of a charging loop at 60-cm separation used in our early testing. We used a different B-field driver for all later tests. The early driver was able to operate the microcontroller at maximum distances of 60 cm, but we did not document its charge rate. Improving this separation distance is a follow-on task. We anticipate achieving about two meters separation or better, but have not as yet made a defensible calculation of the expected maximum range.

The microcontroller has a low power *sleep* mode that is used during the charging period. During sleep, the chip periodically awakens at predetermined intervals to execute the instructions outlined above. The maximum separation of the probe from the reader is determined by the point at which the charging current is less than the sleep current. The values in the table were satisfactory for our proof-of-principle demonstration. However, as indicated in the table, a low-power version of the chip is available that substantially lessens the current draw in sleep mode and would lead to larger physical separation of the probe from the reader.

The important current usage comes from the bottom three entries of Table 1, which give the total charge used by the probe following charging. Their combined charge use is 0.53 millicoulombs, which can be supplied conveniently from a 400-microfarad capacitor. If charged at a 50-microamp rate, the charge time is 40 seconds. Note also that the charge usage for the TDR moisture sensor accounts for only about 3% of the total charge usage, even though its instantaneous current draw is comparatively high.

Table 1. Power Management Parameters. All current draw values are at approximately 5 volts.

Parameter	Current Draw (μ amp)	Time (ms)	Condition
Charge rate	50	N/A	Example value attained in early tests at 60-cm separation from B-field driver. See text.
Microcontroller in sleep mode	20 1*	N/A	Charge rate must exceed this value for a viable system.
Microcontroller active, less all peripherals	50 20*	N/A	With microcontroller program running at 32 MHz clock speed.
Microcontroller active, with peripherals but no sensor or transmitter	440	550	Peripherals active: RF detect, voltage measurement on storage capacitor, reference voltage generated for A/D converter, sensor enable circuit, transmitter enable circuit.
Moisture Sensor	2,250	8	Time for sensor to generate analog output is 5 ms, additional time required for digitizing.
Microcontroller in transmit mode	840	320	Transmitting at 125 kHz with frequency shift keying. Signal received at a 2-meter separation.

* Values indicate the manufacturer's specification for the low-current version of this microcontroller, which was not used.

Figure 3 shows the vertical breadboard (4 x 6 in.) attached to a horizontal interface board, with a TDR moisture probe in front, connected by a long flexible wire. In practice, the electronics and sensor could be colocated. The microcontroller chip is in the socket (the large dark rectangular shape) in the lower left corner of the breadboard. The horizontal dumbbell-shaped object on the top of the breadboard is the magnetic field induction loop on a ferrite core, used for both receiving and transmitting. This particular loop was adapted from a transponder manufactured by TIRIS.^b The TIRIS hardware we worked with has the capability to relay a preprogrammed identification number from a *tag* to a reader by means of passive telemetry. Our work extends and generalizes that concept. Near the left hand of the circuit board, between the antenna and microcontroller, is the energy storage capacitor. Its value was 1,000 microfarads for these tests.

We were able to make all functions of the prototype work simultaneously and self-consistently. This included energy transfer from a loop energizer to the probe (at 60-cm distance) and full function of the probe under control of the microprocessor. All necessary actions were present: acquisition of analog data (moisture) and digitization, transmission of the data back to a receiver (at 120-cm distance, with separate loops for transmitting and receiving), and capture of that data on a data logger. Moisture sensing was quantitative only, as the emphasis has been on the probe system.

b. The TIRIS subsidiary of Texas Instruments is found at www.ti.com/tiris.

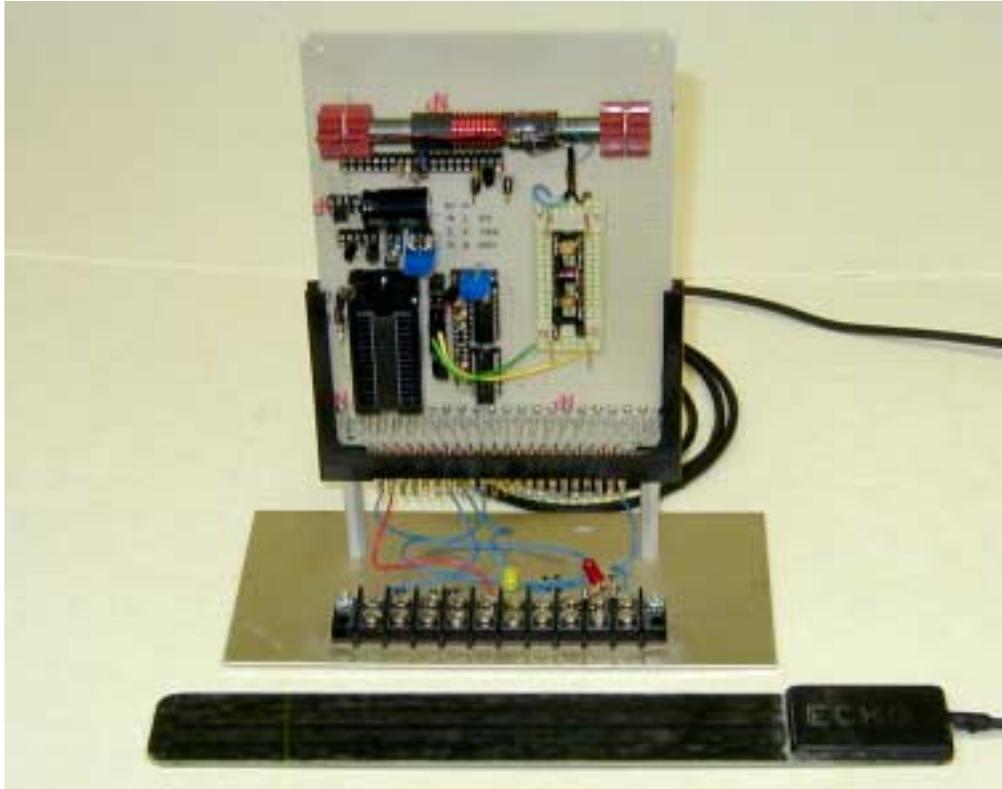


Figure 3. Photograph of the breadboard probe.

Figure 4 shows a real-time data stream plotted by a data logger, generated as follows. A hand-controlled potentiometer has been substituted for the moisture sensor and is a stand-in for a generic analog sensor. The resistance value is varied, and the scope trace so indicates. The inductive input power to the probe has been replaced with a constant 5-volt supply so that the system can trigger repeatedly (our B-field generator has not yet been set up for a pulsed mode that allows for repeated probe transmissions), and the receiver is 120 cm from the probe. The receiving and decoding of the frequency-shift-keyed signal from the probe is fully functional, as described above. The scope trace shows a real-time plot of the digital data being entered into the data logger as the potentiometer is varied by hand, simulating a varying parameter.

We still have work to complete in several areas to prepare a fieldable system. Electrical engineering refinements are required to improve the distance from reader to probe. First, the B-field driver can be improved both in the level of electrical current and the diameter of the coil. Neither of these parameters has been driven to any reasonable engineering limit. Second, a lowcurrent version of the microprocessor is available that draws substantially less current. This is especially important during the sleep period, since that current draw determines the maximum separation between probe and reader. As indicated in Table 1, an improvement factor of 20 is possible by using the low-power version chip. Third, the circuit can be improved in terms of the current draw from the ancillary functions, such as reference voltages and RF detect. These circuit elements need to be powered only at specific times; the present arrangement has them powered at other times as well. We have not produced an engineering estimate of the maximum separation distance, but we anticipate distances of about two meters based on experience with the commercial devices used to communicate identification numbers. Packaging and hardening are also required for a field unit. Ideally, the system would be hardened to the level at which it can be inserted in earthen landfill caps by a simple penetrator rod, and left in place.

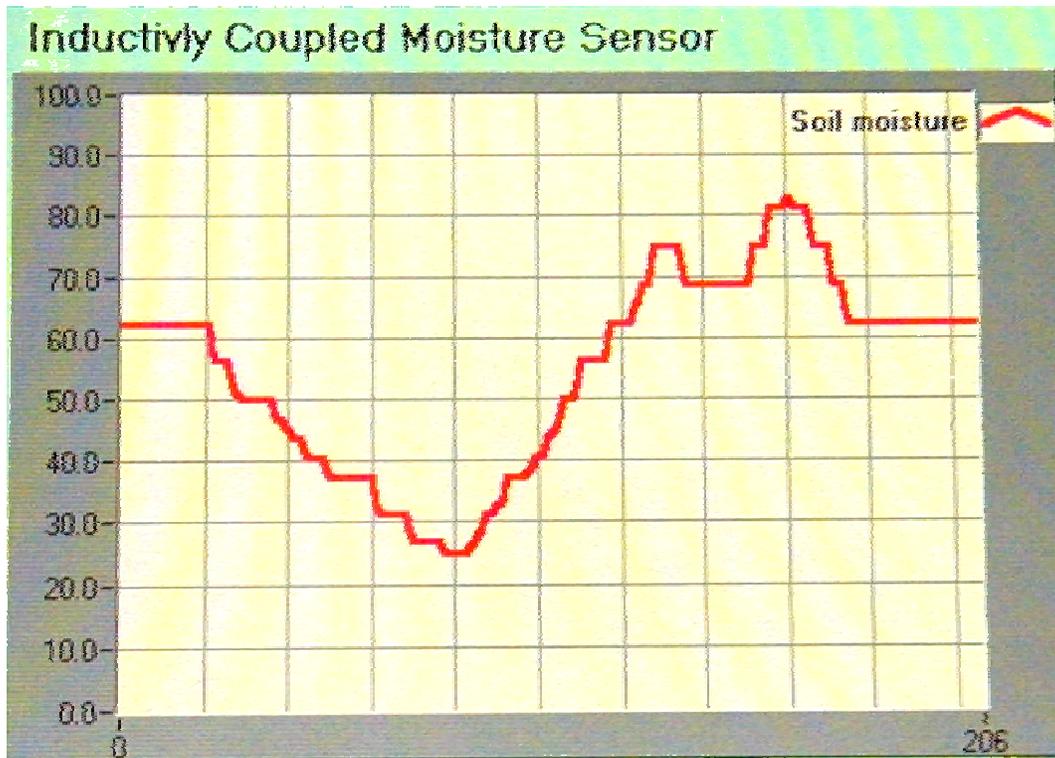


Figure 4. Illustration of a real-time data stream plotted by a data logger.

ACCOMPLISHMENTS

This program offers proof-of-principle demonstration of the PTP concept as a sensor platform. Although the prototype is still being developed, all necessary functions have been generated in a self-consistent parameter set: energy capture and storage by the probe, use of a microcontroller for power management, acquisition of data, and communication to a receiver and database. The digital nature of the system allows numerous possibilities. These include use of multiple probes with one reader reading simultaneously, use of multiple sensors on one probe, instructions delivered to the probe, and data validation within the probe. The concept also has substantial application beyond landfill caps.

REFERENCES

1. Microchip Technology, Inc. "Product Reliability Technical Publication DS11008K," 1998.
2. G. W. Lee and A. L. Ward, "Still in Quest of the Prefect Cap," conference proceedings of "Landfill Capping in the Semi-Arid West: Problems, Perspectives, and Solutions," edited by T. D. Reynolds and R. C. Morris for the Environmental Science and Research Foundation, ESRF-019, Idaho Falls, ID, 1997.
3. W. M. Roggenthen and D. K. Parrish, South Dakota School of Mines, "Factors Affecting Ground Probing Radar at the Radioactive Waste Management Complex Idaho National Engineering Laboratory," prepared for EG&G Idaho, Contract No. C92-17099 (1994).

4. A. R. Von Hippel, editor, "Dielectric Materials and Applications," *The Technology Press of MIT*, John Wiley and Sons, New York.

Advanced Robotic Technologies for Remote Environmental Surveillance and Stewardship

Robots to Measure Hazardous Materials and Contaminated Sites

Mark D. McKay, Ron A. Lujan, and Derek C. Wadsworth

SUMMARY

Advanced technologies for unmanned, autonomous systems are important for future characterization, mapping, navigation, and communication in EM hazardous environments. Remote monitoring techniques may be more cost effective and safer than sending people out to inspect property, particularly when certain areas of a site are inaccessible. They crosscut needs in multiple EM focus areas and programs in which site characterization and monitoring are required, such as decontamination and decommissioning, and they have application in improved navigation of autonomously guided subsurface sensors and improved systems for long-term stewardship of DOE assets. The Cleanup to Stewardship document states that: "...of 109 sites currently expected to require stewardship, 103 are expected to require active stewardship. Active stewardship includes detection monitoring on a continuous or periodically recurring basis.... Sites expected to require active stewardship vary in size and complexity." These sites range from the size of a football field to the size of the state of Rhode Island. The complexity and unstructured environment of the sites require higher levels of intelligence and mobility for future surveillance and monitoring than currently available. The following areas of our investigation are meeting these needs:

- Sensor deployment using multiple agents and improved navigation sensors
- Improved wireless data transfer
- Improved perception of remote environments through charge-coupled device (CCD) sensors.

TASK DESCRIPTION

Sensor Deployment Using Multiple Agents and Improved Navigation Sensors

Safety considerations and increased regulatory requirements for EM programs require sophisticated sensors to detect hazardous materials. These sensors often require precision deployment to guarantee the most accurate detection. Additionally, hazards inherent in the remediation tasks, such as confined spaces, chemical remediation, radiological contamination, and high-radiation fields, add health and safety risks to operators, making remote and automatic deployment of the sensors highly desirable. Because of the unique nature of each activity, a flexible platform that can be reconfigured for each deployment, sensor equipment, and operating condition is needed. To meet these need, we are developing the following:

- A mobile sensor interface design
- Various mobility platforms (ground and aerial) to test sensor, robot, and human interface
- Investigation of distributed robotics for deploying heterogeneous sensors

- Modification, development and or optimization of sensors for field-ready deployment and improved navigation of mobile platforms.

Improved Wireless Data Transfer

Operating remotely controlled equipment in hazardous areas requires a constant transmission of data to communicate control signals, video, etc. This often requires breaching the containment boundary with cables that eventually become contaminated, creating additional waste. One solution to this problem is to develop a wireless communication system capable of penetrating physical structures without requiring line-of-sight contact between operator and manipulator. To meet this need, we are developing a non-line-of-sight wireless communication link capable of transmitting control signals, video, and data over long distances and inside buildings.

Improved Perception of Remote Environments through CCD Sensors

Current handling of radiological materials requires operators to perform work in hot cells. Decommissioning and dismantling hazardous environments and remediating radiation or performing work in other hazardous environments require remote operations. Currently, remote viewing of hazardous environments is with video cameras, which have limited resolution and available field of view. Our research is developing technologies that offer a wide field-of-view (similar to human perception) video system for remote operations. It will enhance operator performance, reduce exposure to hazards, and result in lower operational costs.

It is well-documented that high radiation fields generate a visual effect on modern CCD cameras by over-energizing individual pixels, causing them to display as bright white points. If enough pixels white-out, we get a sparkling or snow effect, commonly encountered when commercial-grade cameras are deployed in radiation fields. It is both intuitive and sufficiently supported by experience to say that the higher the radiation fields the greater the snow effect. The intent of our research is to explore this relationship by exposing a CCD camera to known levels of radiation at various distances from a controlled source and in various orientations to the source. We will use the data gathered to develop a means to quantify the number of pixels over-energized in any given frame of video. This quantified information could in turn be used to estimate the radiation fields to which any given CCD camera is exposed. Successfully quantifying the snow effect on CCDs will offer a method whereby the camera (often much smaller than conventional radiation detectors) can become a radiation detector.

ACCOMPLISHMENTS

Sensor Deployment Using Multiple Agents and Improved Navigation Sensors

Sensor Deployment

We identified two Russian sensor technologies, a gamma locating detector and an isotopic identification instrument, to be demonstrated at the INEEL by the Large-Scale Demonstration and Deployment Program; collaboration is necessary to accomplish the demonstration. We are supporting the integration and are testing the Russian technologies on the iRobot ATRV-Jr robotic platform. This collaboration will allow us to use one of our robotic vehicles to develop the sensor interface for a needed stewardship application. The integrated Russian technologies and robotic platform will be deployed in mid-November at the Test Area North (TAN) TAN-616 facility on the INEEL. Figure 1 shows the robotic platform for this demonstration with the gamma locating detector mounting plate.



Figure 1. ATRV-Jr with a gamma locating detector mounting plate.

We successfully deployed a small unmanned aerial vehicle (SUAV) using a small global positioning system (GPS) navigation package. This low-cost (less than \$500) navigation package, including the GPS unit and servo controller, which weighs approximately 7 oz. During the deployment, a SUAV was air lifted to a starting altitude and position, and the autonomous control system was activated. The SUAV successfully flew the preprogrammed course autonomously while maintaining the desired altitude and relaying real-time sensor data (video and GPS coordinates). Figure 2 shows scenes from this deployment.

Improved Navigation

Sensor deployment is a major component of mobile robot systems. Sensors are typically grouped into two categories, navigation and surveillance. Navigation sensors are those associated with the autonomous guidance of the vehicle. Surveillance sensors are mission specific, and the most difficult to integrate into the robot because of the large variety of interfaces. We designed and tested a generic wireless sensor interface to investigate the idea of deploying a system that could be a stand-alone sensor. The design allows for deployment of a small wireless communications package (cellular, radio frequency, Bluetooth, etc.) and interfaces with a serial or TCP port for the sensor. For sensors without serial output capability, it has an analogue-to-digital converter with a serial or TCP/IP output.

We identified an inertial mass unit (IMU), called the Precision Strike Navigator (PSN), from China Lake as a potential low-cost design for improving navigation, and we arranged an agreement to obtain a prototype for testing. The IMU PSN will be available during first quarter of FY 2001. We are also investigating development of our own low-cost precision navigation system. We purchased and tested a very small ($3/16 \times 3/16 \times 1/16$ -inch), low-cost, low-power tilt sensor/accelerometer. Initial results were very promising. The device will measure the angle of inclination in two axes with a maximum sensitivity of about 0.45 degrees. We conducted tests to determine the accuracy of the sensor on the ATRV-Jr robot. The sensor is self-powered and operated for more than three days. Initial results from the tests show that the sensor is capable of measuring angles from 0 to 90 degrees at 0.5-degree increments. Figure 3 shows the INEEL sensor mounted on a basic stamp development system. The system outputs RS232 data that can be read by any standard serial device.

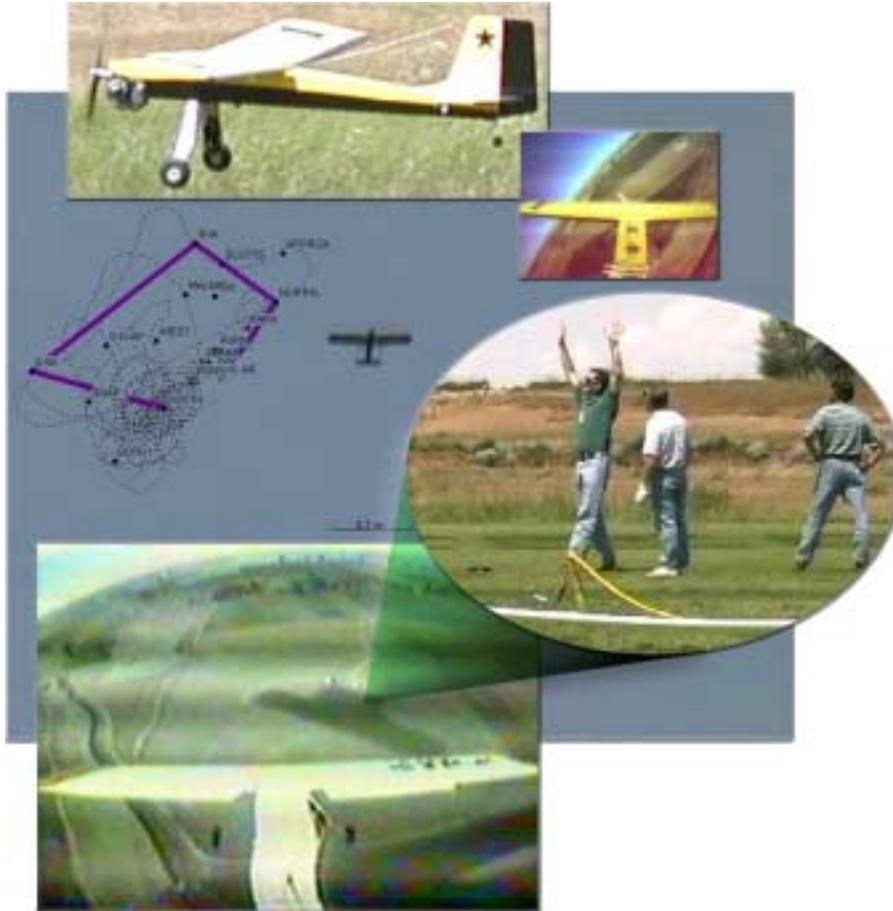


Figure 2. SUAV testing data and images.

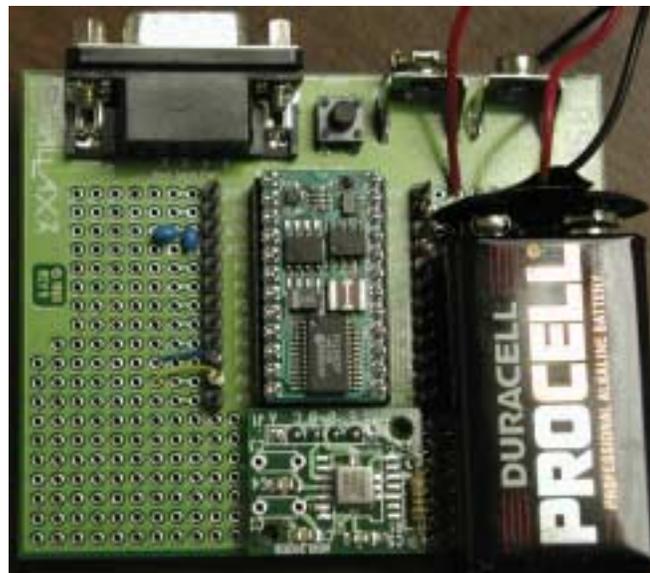


Figure 3. INEEL inclination and accelerometer sensor.

Multiagent

In many situations, multiple robots are an advantage. For example, two robots can be deployed in a cluttered environment and use the sensors from both robots to enhance their capability. We deployed two ATRV-Jr robots in a cluttered environment to demonstrate the benefits of multirobot cooperation. Each robot was equipped with wireless video and sonar sensors. The robots successfully navigated through a laboratory cluttered with obstacles by relying on the data from the sensors of both robots. Figure 4 shows the test setup.



Figure 4. Multirobot cooperation experiment.

Improved Wireless Data Transfer

The goal of this research was to investigate development of non-line-of-sight wireless communications capable of transmitting control signals, video, and data over long distances and inside building structures. Technologies investigated to achieve these capabilities were analog cellular, high radio frequency (RF) local area network, and high RF video.

Cellular Communication

For non-line-of-sight applications requiring outdoor and indoor capability, ubiquitous cellular technology holds the greatest promise for success. In our investigation in this area, we used the commercially available analog cellular phone network covering the entire United States. We designed and prototyped a test system consisting of an analog handheld cellular phone, a handset-to-phone-tone converter, and a PCMCIA cellular modem to test what data rates were most reliable when moving the system from indoors to outdoors. We determined that 1200 baud was the most reliable and robust data rate. Further testing on two INEEL robots followed to determine reliability of robot control using this data link. We successfully operated the robots from indoors to outdoors without vehicle failure or communication dropout. These tests investigated only the control commands of the vehicle, not sensor feedback. Figure 5 shows one of the INEEL robots with the analog cellular prototype used for these tests.

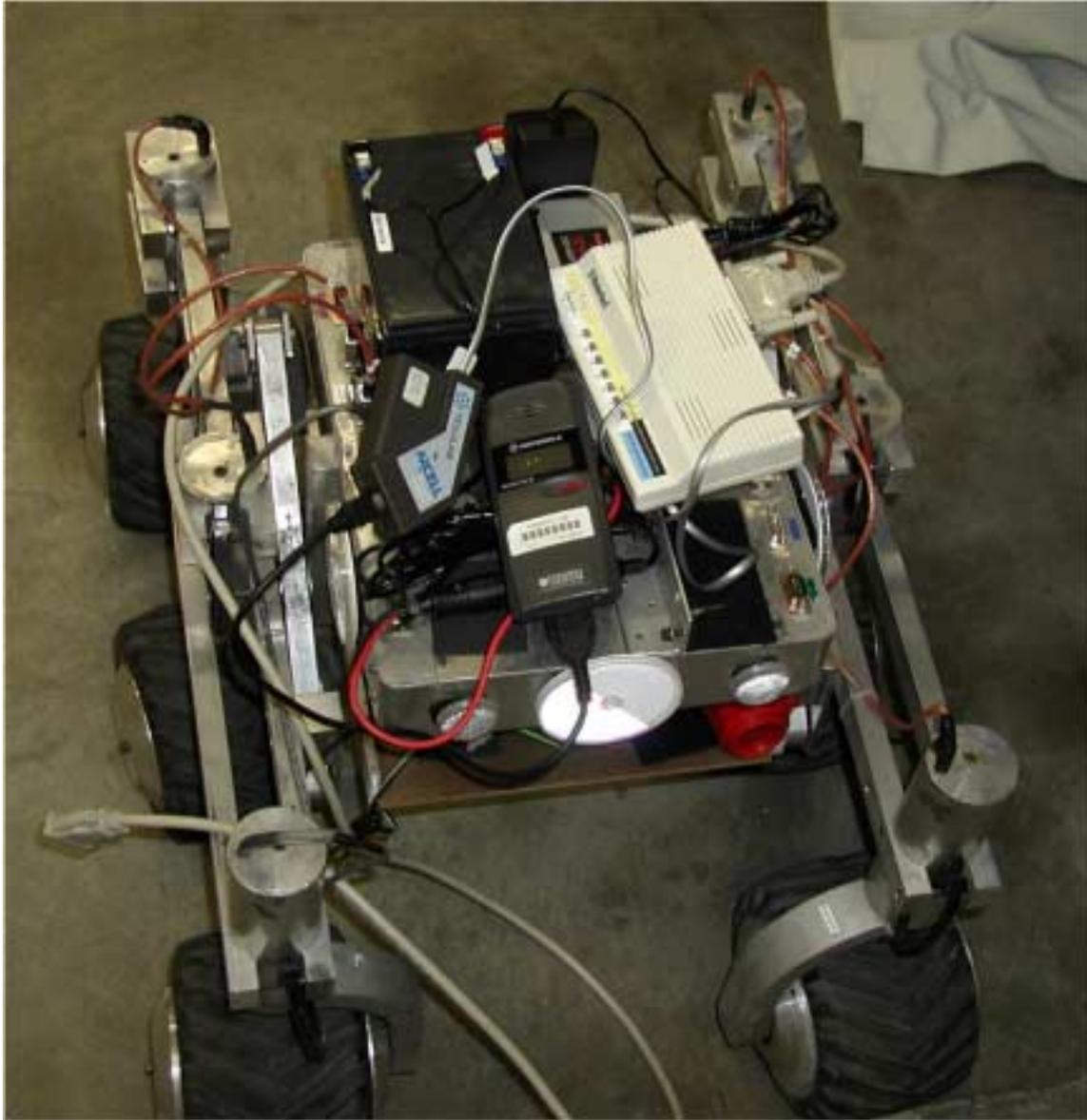


Figure 5. Wireless interface using the cellular communications link on ARC III.

High RF Local Area Network

Streaming real-time video (~15 frames/second) at an image size of 160×128 pixels requires a minimum data rate of 58K baud. We investigated the maximum number of data that could be relayed using the low-bandwidth of the analog cellular 1200 baud data link. We used a high RF local area network and the ATRV-Jr robot to determine the minimum number of video data (picture size) required for teleoperated robot control. From these tests, we determined that an image size of no less than 50×50 pixels at 1/4 Hz is adequate when driving the vehicles approximately two vehicle lengths per image. A commercially available technology is capable of streaming 80×64 images at 1/10 Hz over a wireless CDPD (digital) cellular data link. We plan to conduct further tests of this technology at a 1200-baud rate using the ubiquitous analog cellular network.

High RF Video

We conducted a final investigation on transmitting video by high radio frequency. During the past few years, the INEEL purchased and used state-of-the-art wireless video systems that, nonetheless, are susceptible to dropout and interference and require very directional antennas. During the investigation, we discovered a new technology, available from DTC Communications, Inc., called quality video detect (QVD). It consists of simultaneously sampling multiple receivers at the horizontal line rate of ~15,725 times/sec. The technology promises to optimize signal reception, thus eliminating signal dropout and interference. Testing of this system began in October 2000.

Improved Perception of Remote Environments through CCD Sensors

Wide Field-of-View CCD Sensor

The purpose of this research was to investigate how to best apply current common video camera technology (also known as charge-coupled devices or CCDs) to remote perception. The primary application investigated was real-time observation of a remote area and use of that visual information for a constructive purpose. To gain experience with current CCD technology, we experimented with the use of video camera/television pairs in ground vehicle operation. We selected this for several reasons:

- Most of the equipment was on-hand (vehicle, cameras, televisions), saving significant cost
- Driving is a task most people are intimately familiar with and do every day
- A successful system will apply to remote perception applications such as navigation of a robotic vehicle in hazardous environments.

The information gained directed our selection of currently available components for further investigation.

To that end, we installed five camera/TV pairs on an available all-terrain vehicle (ATV). The cameras were arranged in a semicircular fan and adjusted so their fields of view were continuous. This provided approximately 240 degrees of horizontal view and 90 degrees of vertical. The televisions were arranged in a pattern corresponding to the cameras' positions and were located in a secondary driver's seat in the rear of the vehicle. This seat was covered to force the rear operator to exclusively use the video information to drive the vehicle. Another person rode along in the primary driver's seat during the experiments to observe and ensure safety. It quickly became apparent that a rear view was essential to comfortable operation, prompting installation of a sixth camera, providing a revised total view angle of about 300 degrees. Figure 6 shows various views of this ATV-based system.

We collected experimental data on two pavement courses and several runs in rough terrain (dirt, brush, weeds, and small hills) under a variety of conditions. Results indicate that the video system was useable for most operators, and that performance and confidence increased with both experience and familiarity with the test area. We also observed video quality issues. Small object recognition and distance estimation in the absence of visual clues was difficult for all operators. Of particular interest were identical trials taken with various cameras deactivated. We found that vehicle operation was still reasonably comfortable with the horizontal view reduced to about 150 degrees (three cameras), but reducing it to 80 degrees (front camera only) was not practical.



Figure 6. ATV Test vehicle.

Based on our conclusion that a wider, lesser-quality field of view was better than having a restricted, high-quality one, we decided to invest in a new panoramic camera technology for the next phase of this task. After a vendor search, we ordered cameras manufactured by Remote Reality. We selected these units because each uses a single video signal channel (versus six for our initial test system), which facilitates their use over a wireless link, have a wide field of view (180 and 360 degrees available), and are compact. This facilitates their use in a wide range of applications. The cameras were received in October and will be installed on the vehicle test bed, and we will conduct similar tests.

Radiation CCD Sensor

Our primary object for this research was to gather quantifiable data of the well know sparkle effect that results on video produced from CCD chips exposed to significant radiation fields. The data were obtained at DOE's Laboratory Accreditation Program facility. The facility has two cesium-137 test sources, one 20 curie, one 1,000 curies, which we used to expose a typical commercial grade camera at various distances from the sources. The distances were predetermined to target desired radiation field levels as determined by the inverse square law¹ and a data point measured at 2 m from the sources. Table 1 presents the exposures in the order in which they were performed, which give the true or measured dose-rate actually encountered by the camera, as given by a RO7 Radiation Detector mounted in-tandem with the camera.

Table 1. Actual dose rate encountered by the camera at predetermined radiation field levels.

Exposure	Special Configuration	Curies from Source (Ce-137)	Radiation Level
1	None	20	580 mR/hr
2	None	20	800 mR/hr
3	None	20	5.2 R/hr
4	None	20	10.5 R/hr
5	None	20	50.2 R/hr
6	None	1,000	12.8 R/hr
7	None	1,000	52.7 R/hr
8	None	1,000	105.6 R/hr
9	None	1,000	500 R/hr
10	None	1,000	1,000 R/hr
11	None	1,000	3,200 R/hr
12	Lens removed to maximize approach.	1,000	4,000 R/hr
13	Lens removed to maximize approach.	1,000	1,000 R/hr
14	Lens replaced, camera perpendicular to source.	1,000	140.3 R/hr
15	Lens replaced, camera perpendicular to source.	1,000	113 R/hr
16	Camera perpendicular to source, CCD shielded (independent measurement indicated 85 R/hr at CCD).	1,000	4,000 R/hr
17	Camera perpendicular to source, CCD not shielded.	1,000	4,000 R/hr
18	Camera facing source, low-level sensitivity check	1,000	12.9 R/hr

The intent of the exposures was to gradually step up the dose rate, recording the video image produced at each exposure for approximately 1 minute. Each 1 minute of video produced approximately 1,800 still frames from which we drew random samples to build our visual database. The immediate results of these tests indicate three items of importance.

First, the visual radiation effect on the recorded video was not effected by orientation of the camera to the source. This verified that the interaction of the high-energy photon field with the atoms constituting the CCD did not depend on whether the CCD was normal or perpendicular to the rays of the field but, rather, derived from the probability of encountering an atom based on the volume in space the CCD chip occupied.

Second, the visual effect was completely generated by exposure on the CCD, not on the electronics contained in other parts of the camera housing. We verified this by shielding the CCD chip while exposing the electronics package of the camera to a very high field (approximately 4,000 R/Hr). The visual effect was comparable to that seen at previous exposures taken at radiation fields in the range of 100 R. We then placed a standard radiation detector behind the shielding with the CCD. Its measurement indicates that the CCD was indeed only seeing an 85-R/hr field.

Third, by gradually increasing the exposure levels on the CCD into the thousands of R/Hr and then reversing the process by stepping the exposure back down, we determined that little or no sensitization of the CCD occurred once exposed to high-radiation fields. That is, the lower exposure levels produced visual results directly comparable to those taken at the same exposure levels earlier in the experiment.

We next processed the collection of video frame still images in a digital video editing station. A series of bitmap images showing the exposure effect at various known radiation levels were reproduced on a series of CD-ROM disks and distributed to Remote Video Inspection personnel for visual comparison during future inspections. This visual reference database can begin providing immediate estimations of radiation fields encountered during the course of further remote video inspections. Note that in order to make the best possible comparisons, the iris on the inspecting cameras must be shut down for a short time to allow the visual *sparkle* effect to display against a completely black background, thereby duplicating the video captured during our tests.

The final accomplishment of this task was to create a Microsoft Windows-based program that can analyze a bit-mapped image from the video still frames and rapidly count all the over-charged pixels displayed, quantifying the result of the exposure level. The program also offers a means whereby neighboring pixels *smear*ed with residual energy from the high-energy impact can be eliminated by setting the appropriate brightness threshold. The images shown in Figures 7 through 9 were captured from video recorded during the experiment; the field strength is the gamma radiation field strength in R. The counts are the number of over-energized pixels on the CCD above a background threshold of 80%.

With further development, we could provide near real-time analysis of live video, coupled with a look-up database whereby the number of over-energized pixels are first counted, then compared to results from known radiation levels. The estimated radiation level based on this comparison could then be realized as an on-screen display and recorded with the inspection video.



Figure 7. In a 105-R field, the algorithm counted 113 over-energized pixels.



Figure 8. In a 500-R field, the algorithm counted 532 over-energized pixels.



Figure 9. In a 1,000-R field, the algorithm counted 973 over-energized pixels.

REFERENCE

1. Glenn F. Knoll, *Radiation Detection and Measurement*, Third Edition, John Wiley & Sons, 2000, pp. 497–501.

Isobaric Groundwater Well for Precise Water Level Measurement Relevant to Long-term Surveillance and Stewardship

Measuring Groundwater Aquifer Water Levels More Accurately

Joel M. Hubbell

SUMMARY

DOE depends on accurate data of groundwater elevations to characterize sites, develop site-specific conceptual models of groundwater flow and transport at sites, provide data for predictions of contaminant transport and model calibration, and monitor migration phenomena for long-term stewardship of existing disposal sites and new facilities. Barometric pressure fluctuations influence measured water levels in wells where deep vadose zones or slowly permeable materials overlie unconfined aquifers. These barometric influences are due to the artificial disturbance of installing a well that pneumatically bypasses the vadose zone. Barometric water fluctuations may be severe enough to mask water level trends or pumping test measurements. These barometric pressure fluctuations have been observed in water level measurements obtained from many of the national laboratories including the INEEL, Los Alamos National Laboratory (LANL), Savannah River Site (SRS), and Hanford (tank farms). The purpose of this research and development task is to research, design, build, and test an isobaric groundwater well for obtaining accurate aquifer water levels in unconfined aquifers. These water levels may be used in determining water level trends, groundwater flow rates, groundwater direction, and aquifer hydraulic properties. This isobaric well completion technique seals the interior of the well from atmospheric pressure, and references the water level transducer to the gas phase pressure above the water table (screened across the water table). Water levels were obtained from wells drilled into the Eastern Snake River Plain aquifer to depths of 60 and 180 m below land surface to test the effectiveness of the isobaric technique. Alternating water-level data from a standard and isobaric well completion were collected. Daily water level fluctuations were reduced by an order of magnitude from standard well configuration (± 5.0 cm/d) compared to less than ± 0.5 cm/d compared to using the isobaric technique. The improved precision in the water table data will allow a better understanding of aquifer properties and movement of contaminants in the subsurface for ongoing risk assessment activities, planning and performing remediation actions, and long-term stewardship of the environment at DOE facilities.

TASK DESCRIPTION

Background

DOE facilities require an accurate understanding of aquifer hydraulic properties as determined from the groundwater elevation and from the response of aquifer stress (pumping) tests. Water level elevations can be affected by changes in barometric pressure that are difficult to eliminate by conventional techniques. Current state-of-the-art methods cannot accurately account for fluctuations in the water table caused by these pressure changes, which can cause variations of up to 1 foot. This is most pronounced at sites with deep vadose zones or low hydraulic gradients such as the INEEL. This task will research, design, build, and test an isobaric groundwater well for obtaining accurate aquifer water levels in unconfined aquifers. These water levels may be used in determining water level trends, groundwater flow rates, groundwater direction, and aquifer hydraulic properties.

Successful installation and application of the isobaric groundwater well technique will provide an enhanced determination of hydraulic gradient and aquifer properties at field sites as well as identify and quantify the effects of sources of recharge to aquifers. This task will develop this technique to provide more accurate data about aquifers to improve risk assessment modeling of the time to exposure and location of exposure from current contaminant sources. This technique can provide more accurate aquifer hydraulic property results while using fewer wells, pumping less water, and spending less money compared to current practices.

To prove the practicability of the isobaric groundwater well technique, this task will design, manufacture, install, and test the devices on multiple wells in varying geologic media. The objective is to reduce the water level fluctuation to about 0.01 feet by removing the barometric pressure influence with an innovative technique. Current practices require water level measurements, barometric pressure measurements, and complex, expensive, computer convolution techniques to generate an estimate of the water level. The isobaric groundwater well design automatically removes the effects of barometric pressure fluctuations without requiring further data manipulation. Figure 1 presents data from a well where standard water level measurements were obtained for about a month and was then modified to collect data using the isobaric technique. The data shows a significant improvement in the water level measurements.

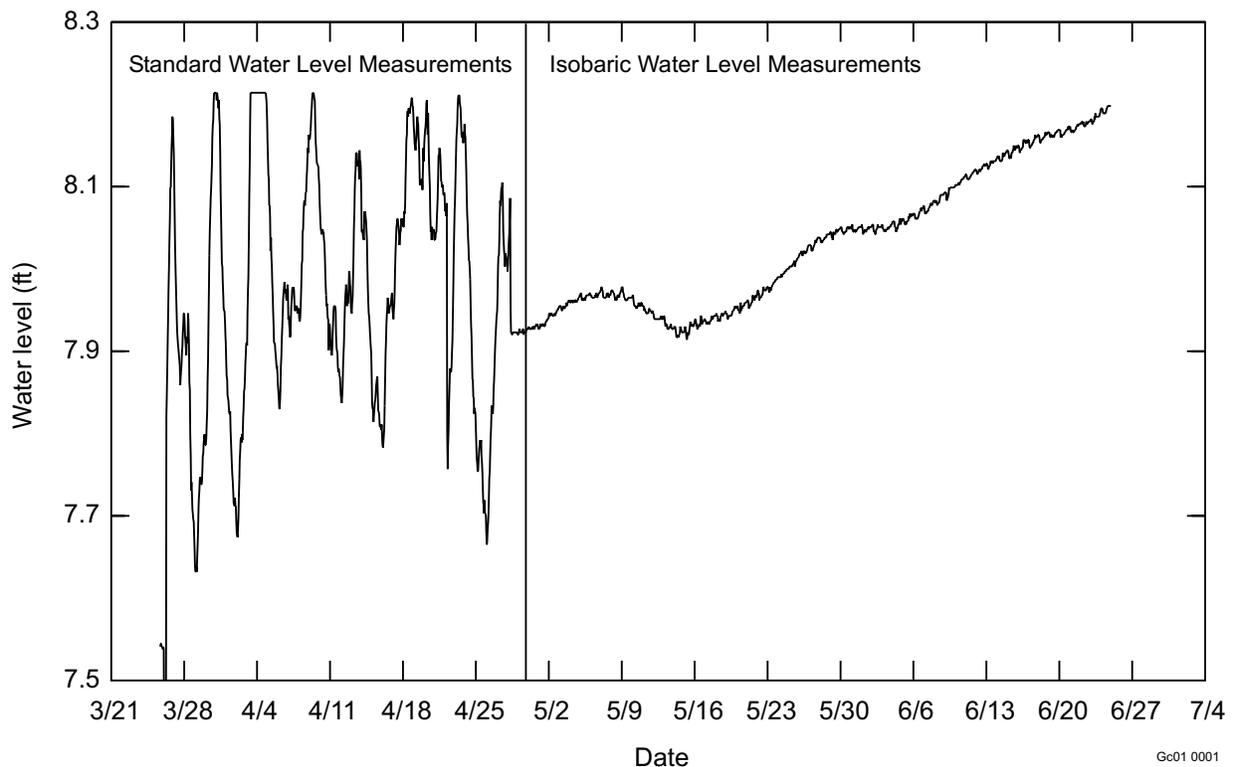


Figure 1. Comparison of water level in a standard and isobaric well.

The isobaric well technique can be used on both groundwater wells and perched water wells in the vadose zone. Following demonstration of this technique, the INEEL expects to transfer this technology to the other DOE sites and the private sector by publishing journal articles and making presentations at conferences.

Task Scope

The overall scope of this task is to (a) determine the theoretical basis and limiting physical factors for use of the isobaric technique for new and existing wells, (b) evaluate the literature to determine locations where this technique is applicable, (c) produce sets of design requirements to build isobaric wells, (d) write procedures for conducting measurements and tests in the field, (e) build new or modify existing wells for testing the isobaric technique, (f) test and demonstrate under variable field conditions, (g) generate a data set of temporal and spatial fluctuations of groundwater hydraulic gradient and flow directions, (h) conduct an aquifer stress (pumping) test using the isobaric technique, (i) submit a paper to a peer-reviewed journal, and (j) conduct tech transfer activities that will include submitting new invention disclosures, preparing patents, and making presentations.

The interaction of water level with external forces of barometric pressure and earth tides was researched to determine if there is new literature pertaining to this topic. Other potential uses of this technique, and sites where the technique will be of use, are being investigated and evaluated. Draft design requirements for constructing, and procedures for conducting measurements have been written for isobaric wells.

Sites at the Radioactive Waste Management Complex (RWMC) and Test Area North (TAN) on the INEEL were evaluated to determine the best location for setting up and running tests on the hydraulic gradient portion of the isobaric investigation. Representatives of Environmental Restoration's (ER's) Waste Area Groups 3 (TAN) and 7 (RWMC) were contacted to discuss using existing wells. The TAN site was chosen to run the hydraulic gradient portion of the tests. ER activities will be coordinated with the isobaric data well modifications and subsequent data collection.

A well site visit was performed at TAN to evaluate the requirements for performing the field hydraulic gradient test on the designated wells. As anticipated, three of the four wells can be used without modification, but the last well (TAN 4) will have to be modified. Initial tests will be required on TAN 4 and one other well to ensure they will function as isobaric wells. Several alternatives have been evaluated to determine the most applicable modification to these wells. One of the proposed modifications was sufficiently novel to warrant preparation of an invention disclosure for the technique. An outline of test/equipment requirements and procedures was prepared to guide the field tests.

A presentation on the isobaric investigation was presented to the ESRC peer review group in July. The feedback on this work was very supportive. Task personnel have been working with representatives of the University of Idaho and the Idaho Water Resources Research Institute to develop applications for this technique.

Initial follow-up contact was made with Pacific Northwest National Laboratory to discuss future interactions and uses of the isobaric well at Hanford. Discussions have been initiated with WAG-10 to use the isobaric well technique developed at the INEEL at other selected sites. This work will complement the work performed on this task.

Development of Technologies and Intellectual Properties

A patent application was prepared and submitted for consideration to the U.S. Patent and Trademark Office for a tensiometer that will use the isobaric technique for obtaining more accurate soil water potential measurements in the vadose zone.

ACCOMPLISHMENTS

Our accomplishments during FY 2000 are as follows:

- A patent application was prepared and submitted for consideration to the U.S. Patent and Trademark Office for a tensiometer that will use the isobaric technique for obtaining more accurate soil water potential measurements in the vadose zone.
- An invention disclosure was drafted for a well sealing technique that can be used with the isobaric well. This technique will be useful in new and existing wells and will have minimal impact on well construction. It will be less complicated to install than existing sealing techniques and will not significantly interfere with standard uses of the well.

REFERENCES

None

Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes

Identifying Microbe Chemical Signatures More Easily and Quickly for Remediation

Jani C. Ingram, R. Michael Lehman, William F. Bauer, F. S. (Rick) Colwell, A. D. Shaw

SUMMARY

In situ bioremediation—the ability to use naturally occurring microbes to remediate the effects of man-made contamination—is an important research thrust for the EM mission with significant potential to reduce overall cleanup costs. Researchers need improved, direct methods for detecting and characterizing microorganisms in situ; they must be able to understand which microbes already exist in the target site in order to optimally take advantage of those microbes for cleanup.

Current microbial characterization methods require researchers to extract microbes from the surface of the samples and culture them in the laboratory. This research task will explore the possibility of using secondary ion mass spectrometry (SIMS)—a surface chemistry detection technique—to identify microbes in situ by examining their outer cell membranes. This technique is already being used on the minerals and plants that the microbes live on. Enhancing SIMS for this purpose could significantly advance microbial ecology studies because it will not separate microbial cells from the mineral surface and can be coupled with mineralogical analyses. This new tool should promote better understanding of bioremediation processes through in situ characterization.

Our approach uses static SIMS to probe the top layers (membrane) of intact microbial cells. We are using two SIMS instruments built in-house: a triple quadrupole, and an ion trap mass analyzer. These instruments are unique, built on several SIMS research and development (R&D) projects at the INEEL over the past 15 years. Unlike most microbiological characterization methods, our approach does not require the microorganisms to be extracted from the mineral surface, thus providing an in situ means for identifying microorganisms. This capability could advance microbial ecology studies because the approach does not separate the microbial cells from the mineral surface, rather, it minimizes the need for manipulations that depend on nuances of cell structure or physiology; and it can couple with mineralogical analyses. Thus, development of this methodology will offer a tool to better understand bioremediation processes through in situ characterization.

Our objectives were to (a) generate MS^n approaches and protocols for ionic fragmentation of the diagnostic ions, (b) develop surface treatment approaches for optimizing SIMS detection, (c) make software modifications to the ion trap SIMS operating systems to allow for longer ionization and trapping times, and (d) begin testing SIMS as a tool for characterizing microbial species of interest to bioremediation efforts. During the first 6 months of this task we initiated objectives a, c, and d; objective c is complete and objectives a and d are in progress.

TASK DESCRIPTION

Introduction

The surface structures of microbial cells are important because they are in direct contact with the external environment and are highly dynamic in order to withstand environmental changes. These

alterations in the surface chemistry of the cells provide a means for gaining insights into microbiological processes occurring in the environment. Owing to its importance, characterization of the microbial cell surface chemistry is an expanding field in microbiology. A widely used approach in the study of the surface chemistry of microbial cells is to use staining techniques coupled with various microscopy approaches for probing specific components of the microbial cells. For example, negative staining techniques coupled with electron microscopy have been extremely useful in studying the ultrastructure of flagella, fimbriae, F-pili, fibrils, and S-layers.¹ By using these visual techniques, much can be learned about the physiology of the cells, with the various stains providing insight into specific components of the microbial cells. These reaction chemistries are not always specific, however, and can be hampered by unwanted side reactions occurring between the stain and other components within the cells.

Another widely used approach to characterize the surface chemistry of microbial cells is to extract the components of the cell membrane, then to perform chemical analyses on the extract. With the maturity of analytical techniques to provide specific identification of highly complex, biochemical compounds, much has been learned concerning the constituents of the microbial membrane. A wide variety of mass spectrometry techniques have been developed² capable of determining species as small as the electrolytes within the cells³ to as large as proteins and polypeptides.^{4,5} The major limitation to this approach is that the components of interest must be extracted from the cells and isolated from the cell matrix before analysis, which precludes the possibility of investigating the microorganisms under near in situ conditions.

Clearly, direct analysis of microbial cell surface chemistry is desired. A variety of surface analysis techniques exist; however, many of those techniques, such as energy (or wavelength) dispersive x-ray spectroscopy and Auger electron spectroscopy, provide only elemental information, which has limited application for characterizing biochemical systems. In contrast, x-ray photoelectron spectroscopy (XPS) can give more than just elemental composition and has been used to investigate the chemical composition of the microbial cell surface.^{6,7} XPS is capable of interrogating the surface of intact cells, but is limited in that it provides chemical state or oxidation information that is reflected by small shifts (less than 1 eV) in the binding energies of the core electrons. These small shifts are difficult to resolve instrumentally. Thus, interpretation of the spectra of organic compounds is limited to identifying classes of organic compounds by this technique.⁸ Determination by XPS of specific molecular information about the cell surface chemistry is problematical.

Some surface analysis techniques, however, have the capability to more specifically characterize the surface chemistry of intact microbial cells. Infrared spectroscopy (IR) is a vibrational spectroscopy that interrogates molecular bonding. Because the energies of molecular bonds in biochemical systems are very sensitive to changes in chemical structure, IR is very useful for identifying specific molecular species, and to potentially provide molecular compositional information from intact microorganisms has been demonstrated. Using synchrotron radiation (SR) as the excitation source is particularly promising, as the SR source provides improvement in the signal-to-noise ratio over that of FTIR spectra recorded from a conventional blackbody source.⁹

Our approach is to use static SIMS equipped with a molecular primary beam. In static SIMS, the surface is interrogated by bombardment with particles (a primary beam of molecular ions) that dislodge molecular species from the solid, ejecting (or sputtering) them into the gas phase where the ionized molecules and their fragments can be mass analyzed. These ionized pieces of the surface reflect a detailed picture of the surface chemistry of the solid.¹⁰ An advantage of SIMS relative to other surface analysis techniques is that it is extremely sensitive; SIMS has the capability of detecting molecular species at 0.001 monolayer levels.¹¹ Although mainly used by the semiconductor and polymer industries, some initial effort has applied SIMS to the study of biological samples. Winograd's group has demonstrated that SIMS can interrogate the exposed head groups and tail groups of phospho-lipid membrane molecules in freeze-fractured red blood cells.¹² These results demonstrate the utility of SIMS for not only chemical

analysis but also for determining the molecular orientation of cell surface molecules. Todd and coworkers used SIMS to map phosphocholine in rodent brain tissue.¹³

We use a molecular primary beam for bombarding the sample.^{14,15} We use ReO_4^- in place of the conventional Cs^+ or Ga^+ atomic beams typical of commercial SIMS instruments. Our previous studies with molecular primary beams^{16,17,18} show an increase in sensitivity by a factor of 10 to 30. This becomes increasingly important as the surface concentration of the analyte decreases, and, on environmental samples, we anticipate the need to detect submonolayer concentrations. Schamberger and coworkers report using SIMS with a Cs^+ primary ion beam to study microbial cell surfaces.¹⁹ Limitations relating to the cationic molecular fragments produced by the Cs^+ beam made it difficult to observe quantifiable differences in the SIMS spectra of various microbial species. Our work indicates that the ReO_4^- primary beam can overcome these limitations.

Experimental Section

Microbiology

We analyzed 38 bacterial strains by both SIMS and the Sherlock Microbial Identification System (MIS; MIDI, Inc., Newark, DE, USA). The purpose of the MIS analyses was to determine the fatty acid methyl ester (FAME) profiles of each bacterium. The bacteria were obtained either from an established culture collection and initially cultured on the recommended solid media, or isolated from environmental samples on R2A solid media, as noted in Table 1. With one exception, all organisms were then grown aerobically on trypticase soy broth-agar (TSBA) and harvested for FAME analysis as recommended by the MIS operating manual. We determined taxonomic affiliations using the MIS library for the *aerobe method*. Similar cultures grown on TSBA were harvested for SIMS analyses. The one exception was the obligate anaerobe, *Methanoculleus marisnigri*. This organism was obtained from the Oregon Collection of Methanogens and cultured in the recommended anaerobic liquid media. *Methanoculleus marisnigri* was then prepared for analysis by pelleting by centrifugation and washing with phosphate buffer. We used the pellet for both SIMS and FAME analysis.

Table 1. Information on microorganisms.

Isolate	Organism	Identification	Source	Cell Wall
1	<i>Paenibacillus macerans</i>	American Type Culture Collection (ATCC) 49035	culture collection	gram positive
2	R2A Bug	<i>Bacillus filicolonicus</i> (0.259)	media contaminant	gram positive
3	USGS103-Y	<i>Arthrobacter ramosus</i> (0.706)	groundwater	gram positive
4	USGS103-Z	<i>Bacillus atrophaeus</i> (0.605)	groundwater	gram positive
5	TAN33 Matt-F	No database match	basalt core	unknown
6	TAN33 Matt-H	No database match	basalt core	unknown
7	TAN33 Matt-K	No database match	basalt core	unknown
8	<i>Staphylococcus aureus</i>	<i>Staphylococcus aureus</i> (0.797)	lab contaminant	gram positive
9	TAN33 MLS-49	No database match	groundwater	unknown
10	TAN33 MLS-52	No database match	groundwater	unknown
11	TAN33 MLS-73	No database match	groundwater	unknown
12	TAN33 MLS-88	No database match	groundwater	unknown

Table 1. Continued.

Isolate	Organism	Identification	Source	Cell Wall
13	<i>Methanoculleus marisnigri</i>	Oregon Collection of Methanogens	culture collection	Archaea
14	TAN37 38-1	<i>Pseudomonas syringae</i> (0.515)	basalt core	gram negative
15	TAN37 43A-9	<i>Arthrobacter globiformis</i> (0.422)	basalt core	gram positive
16	TAN37 43B-1	<i>Rhodococcus sp.</i> (0.042)	basalt core	gram positive
17	TAN37 43B-2	<i>Rhodococcus sp.</i> (0.010)	basalt core	gram positive
18	TAN37 43B-3	<i>Rhodococcus luteus</i> (0.715)	basalt core	gram positive
19	TAN37 43BW-1	<i>Pseudomonas putida</i> (0.257)	groundwater	gram negative
20	TAN37 43BW-6	<i>Pseudomonas fluorescens</i> (0.487)	groundwater	gram negative
21	TAN37 43BW-11	<i>Pseudomonas alcaligenes</i> (0.147)	groundwater	gram negative
22	<i>Stenotrophomonas maltophilia</i>	ATCC 13637	culture collection	gram negative
23	<i>Pseudomonas stutzeri</i>	ATCC 17588	culture collection	gram negative
24	<i>Rhodococcus globerulus</i>	ATCC 19370	culture collection	gram positive
25	<i>Alcaligenes xylosoxydans</i>	ATCC 15173	culture collection	gram negative
26	<i>Agrobacterium tumefaciens</i>	ATCC 15955	culture collection	gram negative
27	<i>Hydrogenophaga pseudoflava</i>	ATCC 33668	culture collection	gram negative
28	TAN37 18BW-2	<i>Hydrogenophaga pseudoflava</i> (0.935)	groundwater	gram negative
29	TAN37 18-3	<i>Acinetobacter genospecies 9</i> (0.486)	basalt core	gram negative
30	TAN37 18-7	<i>Sphingobacterium spiritivorum</i> (0.218)	basalt core	gram negative; sphingolipids
31	TAN37 18-9	<i>Rhodococcus equi</i> (0.013)	basalt core	gram positive
32	TAN33 Matt-A	<i>Rhodococcus sp.</i> (0.227)	basalt core	gram positive
33	TAN33 Matt-B	<i>Brevundimonas vesicularis</i> (99.3%) ²	basalt core	gram negative
34	TAN33 Matt-C	<i>Sphingomonas macrogoltabidus</i> (97.8%) ³	basalt core	gram negative; sphingolipids
35	TAN37 Matt-U	<i>Rhodococcus erythropolis</i> (0.239)	basalt core	gram positive
36	<i>Agrobacterium tumefaciens</i>	ATCC 15955	culture collection	gram negative
37	<i>Arthrobacter globiformis</i>	ATCC 8010	culture collection	gram positive
38	<i>Sphingomonas capsulata</i>	ATCC 14666	culture collection	gram negative; sphingolipids

SIMS Instrumentation

The SIMS instrument used in these studies is described in detail by Appelhans et al.²⁰; a brief description is provided here. The instrument uses ReO_4^- at 5.25 keV as the primary bombarding particle, which is produced by heating an $\text{Eu}_2\text{O}_3/\text{Ba}(\text{ReO}_4)_2$ ceramic in vacuum.¹⁵ We synthesized the ceramic in our laboratories and processed it in a form that could be used as an ion source. The ion gun was typically operated at 250 pA. Acquisitions required less than 100 s, and a typical sample had an area of about 0.06 cm^2 ; thus, primary ion doses were less than $2.6 \times 10^{12} \text{ ions/cm}^2$, which is below the commonly accepted static SIMS limit.²¹

We have developed patented methods to overcome surface charging in which the extraction of positive and negative charge is balanced so that the sample, on average, gains no net charge.^{20,22} This technique, when used with the ReO_4^- primary ion gun, mitigates charge buildup on the surface of the sample and thus permits facile analysis of electrically insulating samples such as minerals and leaves. We used two different mass spectrometers in this work. We used a triple quadrupole system (2 to 600 amu) manufactured by Extrel (Pittsburgh, Pennsylvania) and modified in our laboratory. The base pressure in the instrument was typically 3×10^{-7} torr. The quadrupole was tuned for unit mass resolution and optimum sensitivity for m/z 81⁻ and 198⁺ in the SIMS spectrum of tetrahexyl ammonium bromide. We also used a modified Varian Saturn 2000 ion trap mass spectrometer (Walnut Creek, California) adapted for secondary ion mass spectrometry. The Varian-based IT-SIMS has not been described previously in the literature, but is very similar in design and operation to the Finnigan-based IT-SIMS instrument described in detail by Groenewold et al.²³ Briefly, the instrument is equipped with a ReO_4^- primary ion gun and an offset venetian dynode/multichannel plate detector system housed in a custom-fabricated vacuum chamber.

Statistical Analysis

Multivariate analysis methods²⁴ commonly used to determine analyte concentrations in overlapped spectra include classical least squares,²⁵ partial least squares,²⁶ principal component regression,²⁷ and occasionally, neural networks.²⁸ Multivariate analyses have been successfully used for interpretation of mass spectra of microorganism-related chemistry.^{29,30}

After the initial attempts at principal components analysis (PCA), using grams/32 with the PLS/IQ package, we focused on finding the optimum mass ranges and optimum methodologies to design a methodology that for proof-of-principal could be used to classify bacteria based on their SIMS spectra. One problem has been that because the number of spectra is relatively limited for the calibration set (224) and the number of microbial types is large, there is currently no really good set of spectra to use as a verification set. For development, our initial primary focus was on the gram negative and gram positive character of the microbes. We generally used the correlation coefficient of a principal components analysis/regression (PCA/R) or a partial least squares (PLS) calibration for gram positive bacteria as an indicator. For the initial calibrations, we selected factors using the F-statistic at $p = 0.05$ applied to the Eigen values. This worked quite well for the PCA/R calibrations; however, this was not as useful for the PLS and the PLS factors we usually picked by the minimum calculated F-statistic. In the final stages, we only performed the more rigorous selection of factors based on a cross-correlation analysis—using the calibration set as the verification set by recursively performing the calibration with $n-1$ spectra and using the i th spectrum as the unknown—because the calculation time was excessively long. We performed calculations in MatLab using the PCA/R and PLS routines available in the chemometric toolbox for MatLab by Richard Kramer. The routines in the toolbox allow one to select either the nonlinear iterative partial least squares or decomposition algorithms.

We made several attempts to determine which masses were best for determining the gram negative/positive nature of the microbes from the SIMS spectra. The major downfall of this type of analysis is how to normalize the spectrum. We achieved some limited success by using a moving window of 3, 5, 10, 20, etc., points (m/z 's). Each window was normalized to the maximum value and a PLS performed using the entire data set or a subset in which potential outliers were removed. The net result of this was that the best correlation to the gram +/- was in the positive ion spectrum in the m/z range of ~70–110. We noted that with the smaller windows, correlation centers around the common fatty acid ions in both the positive and negative ion spectra. Close examination of the spectra revealed that in the negative ion mode, the spectra of Paenbacillis and R4A consisted primarily of noise, so subsequently we considered the spectra for these bacteria as possible outliers.

Results

This section describes the task results obtained during the last two quarters of FY 2000. These results are described in terms of the objectives set at the start of the program: (a) to generate MS^n approaches and protocols for ionic fragmentation of the diagnostic ions, (b) to develop surface treatment approaches for optimizing SIMS detection, (c) to modify software of the ion trap SIMS operating systems to allow for longer ionization and trapping times, (d) to begin testing SIMS as a tool for characterizing microbial species of interest to bioremediation.

Objective A: Generation of MS^n Approaches

An objective of this task was to develop MS/MS methods for identifying diagnostic ions present in the microbial cell membrane. The purpose for developing MS^n methods is to enable specific identification of chemical species, which is important in chemical characterization of microorganisms. In our initial work, we observed cations at even masses in the SIMS data of intact microorganisms. These even mass cations are typically associated with organic amines, which suggests that fragment ions associated with proteins may be present in the SIMS cation spectra. An example of this is the comparison of SIMS spectra of two strains of *Shewanella alga* (BrY and adhesion-deficient RAD20), which differ mainly in their ability to bind to ferric oxides. Biochemical evidence showed that the BrY strain contained proteins on the cell surface that enabled adhesion to occur, whereas those proteins were absent in the adhesion-deficient RAD20 strain. The SIMS cation spectra of these strains shows marked differences in the even mass ions, which suggests that the differences in protein composition of these two strains is reflected in the SIMS data.

Based on these observations, we collected SIMS data on 20 amino acids as a start for detecting protein development. Overall, we observed good spectral signatures of the amino acids in the single MS of the SIMS data. A second stage of MS was performed (MS/MS) on the molecular ions ($[M+H]^+$) of the amino acids. We observed (see example in Figure 1) that $[M+H]^+$ could be fragmented by a loss of formic acid, which could be used as a diagnostic for identifying the amino acids present. Our next step is to analyze peptides (which we are procuring) by SIMS to determine how well SIMS can identify the amino acids present in the various peptide compounds.

Objective B: Development of Surface Treatments

We have not begun work on this objective. We plan to begin surveying acid/base treatments to obtain improved ion generation and some specificity for particular groups of chemical species.

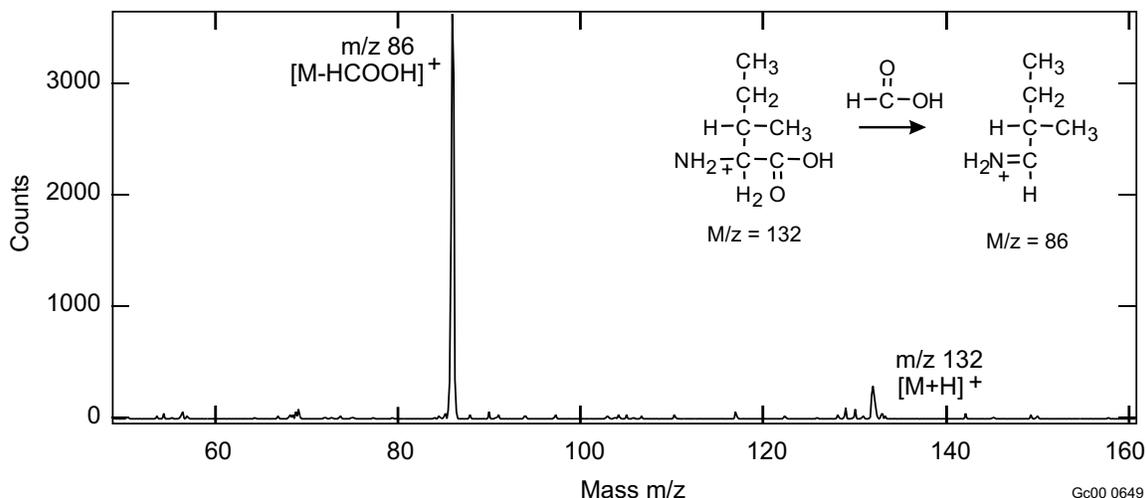


Figure 1. MS/MS of isoleucine by ion trap SIMS.

Objective C: Software Modifications

The objective to modify software for the ion trap SIMS data systems to achieve longer ionization times (necessary for some of the ion trap SIMS analyses) was accomplished by John Olson, who has been working on instrument development of the IT-SIMS system for the past few years. Using information gained through a nondisclosure agreement with Varian, the total time that can be used for scan functions, which includes the ionization time, has been extended from ~2 to ~130 s. This allows for virtually any ionization time needed for IT-SIMS. This capability also allows for longer collision-induced dissociation (CID) times. Longer CID times allow the use of lower dissociation energy to fragment the ions, which is an advantage when investigating less stable ions in a MS/MS analysis. This task was completed.

Objective D: Testing SIMS for Microorganism Analysis

In this study, we compared the SIMS data of 38 microorganisms to fatty acid profiles determined by MIS. The results indicate that surface bombardment using a ReO_4^- Primary beam cleaves the ether linkage characteristic of Archea at the glycerophosphate backbone of the phospholipid components of the cell membrane. Similar cleavage at the ester linkage in eubacteria was also observed. This cleavage enables direct detection of the fatty acid conjugate base by static SIMS. An example of SIMS' detecting fatty acids by SIMS is shown in Figure 2, which compares the anion SIMS spectrum of *Methanococcus marisnigri* to the fatty acid profile generated by MIS. The labeled anions in the SIMS spectrum correspond to the fatty acids described in the fatty acid table. The results indicate that the fatty acids present at mid to high mole% (as determined by MIS) are also observed in the SIMS anion spectrum. SIMS does not detect those fatty acids present in trace amounts (less than 1 mole%).

In addition to detecting fatty acid, we performed partial least squares analyses of the SIMS data to determine if SIMS were capable of differentiating gram positive and gram negative bacteria. We hypothesized that since the differences in gram positive and negative bacteria is due to differences in their cell wall chemistries, SIMS would be capable of interrogating this outer region of intact bacteria. Partial least squares (PLS) regression analysis ($R^2 = 0.988$) for gram positive/negative character of the 38 different bacteria using the SIMS anion spectra resulted in a clear grouping of the gram-positive and gram-negative species (see Figure 3). The first PLS factor has many of the ions expected from membrane fatty acids that would be more prevalent in the spectra from gram negative bacteria (see Figure 4).

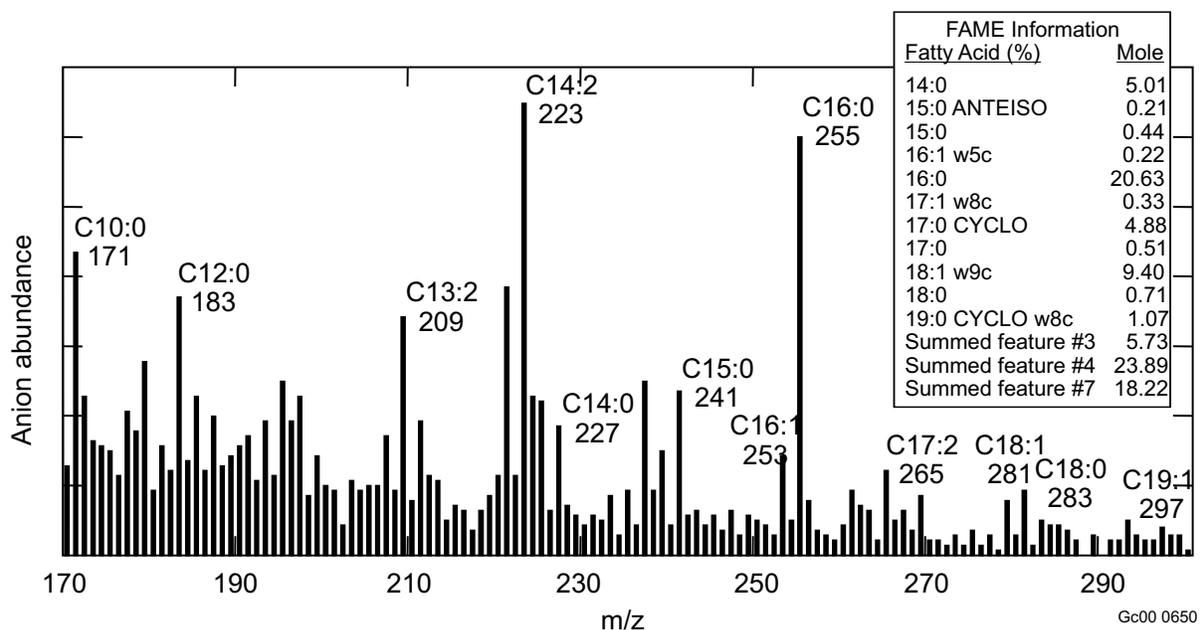


Figure 2. Under: anion SIMS spectrum of *Methanococcus marisnigri*; Over: Fatty acid methyl ester profile of *Methanococcus marisnigri*.

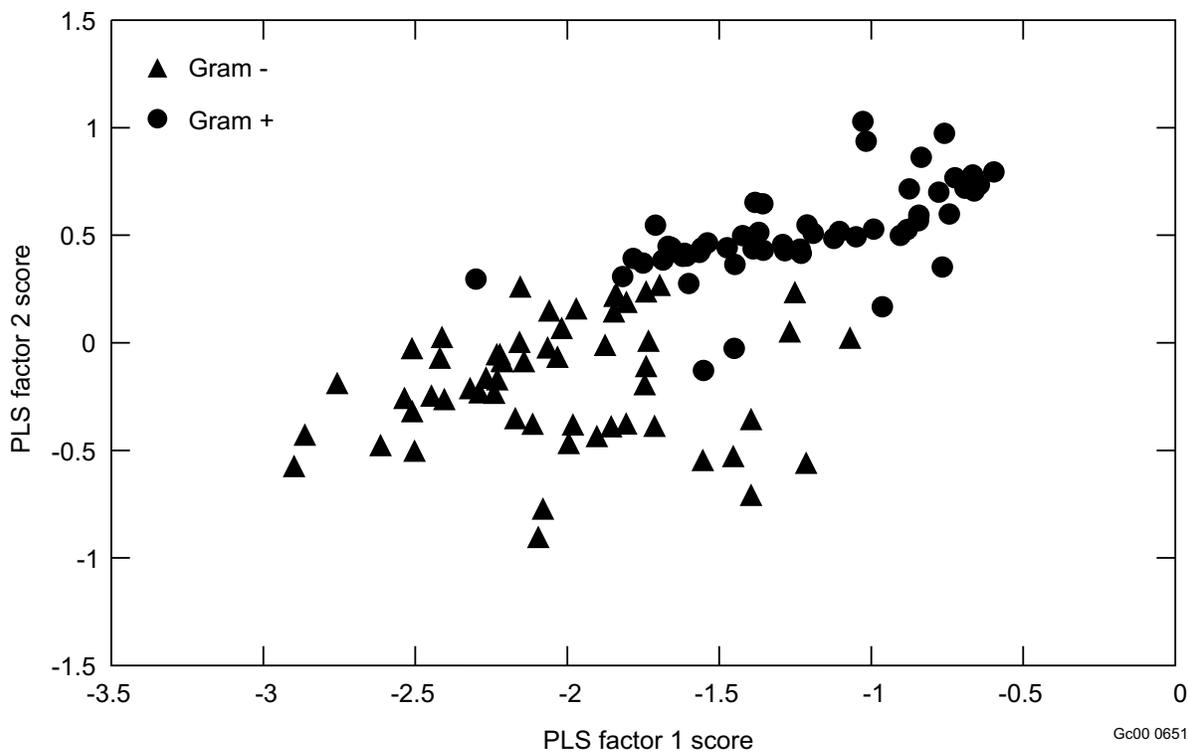


Figure 3. Partial least squares analysis of SIMS data demonstrating statistical grouping of Gram positive and negative bacteria.

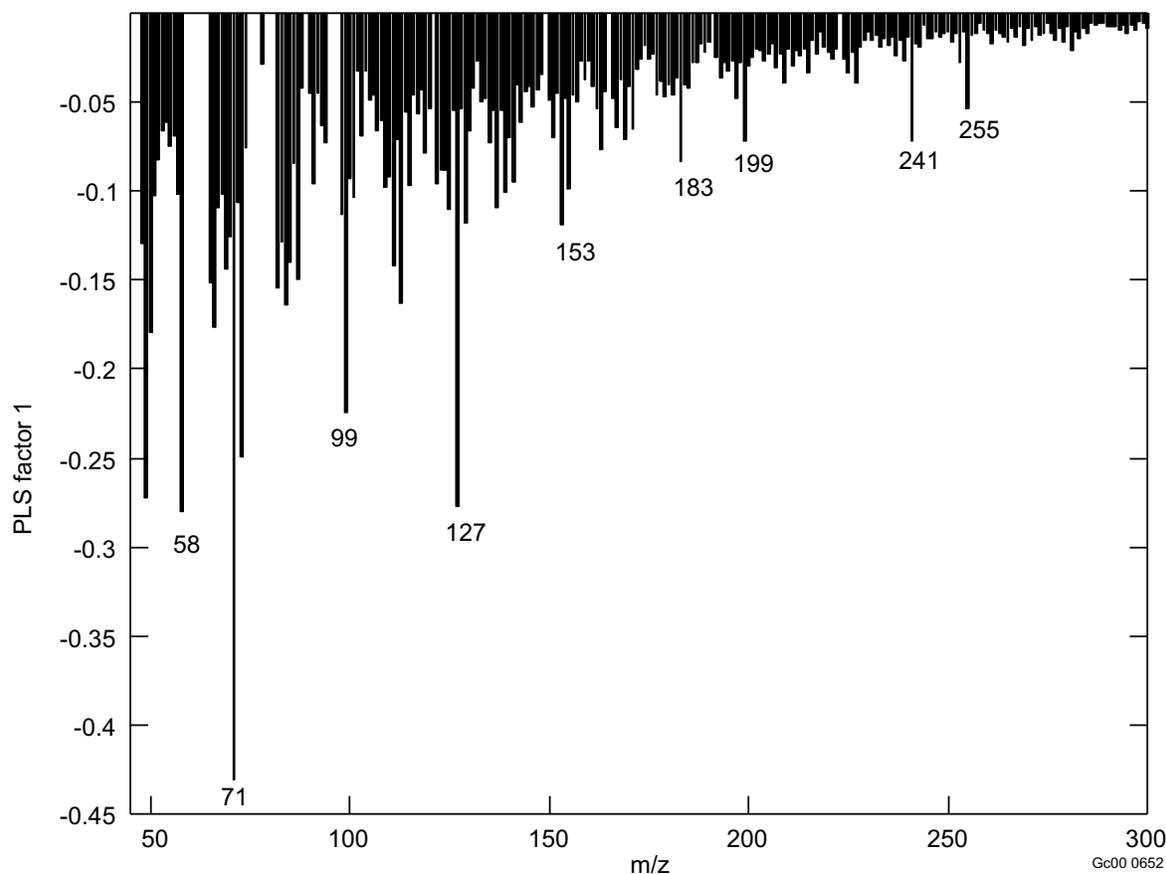


Figure 4. The first PLS factor for the Gram negative bacteria plotted versus m/z which contains a number of fatty acid-related ions.

In our next experiments we will begin analyzing mixed cultures by SIMS, starting with two microorganism systems. Additionally, we will begin assessing the minimum detection limits of SIMS for microbial analysis. This information will enable a clearer understanding of how SIMS can be used for characterizing environmental and/or bioremediation activities of microorganisms.

ACCOMPLISHMENTS

The INEEL has advanced toward having the unique capability to detect and identify microorganisms using SIMS. Results of this FY 2000 research demonstrate that SIMS can provide fatty acid chemical information about the cell membrane of microorganisms comparable to the information obtained from the microorganism identification system (standard technology used by microbiologists), which is a much more labor-intensive approach. Further, the preliminary amino acid work suggests that SIMS has some capability for detecting and identifying proteins present in the cell membrane, which can be very useful chemical signatures for use as biomarkers. Additional work in this area is required to assess the extent to which SIMS can be used for protein analysis. Overall, these results suggest that SIMS can interrogate the cell surface chemistry. We plan to investigate detection limits and how specific microorganisms can be typed (groups, species, subspecies) by SIMS.

REFERENCES

1. P. S. Handley, "Negative Staining," in N. Mozes, P. S. Handley, H. J. Busscher, P. G. Rouxhet, (Eds.), *Microbial Cell Surface Analysis Structural and Physicochemical Methods*, VCH Publishers, New York, 1991, p. 65.
2. C. Fenselau, (Ed.), "Mass Spectrometry for the Characterization of Microorganisms," *ACS Symposium Series 541*, ACS, Washington D.C., 1994, see chapters within.
3. M. L. Pacholski, D. M. Cannon, Jr., A. G. Ewing, and N. Winograd, "Molecule Specific Imaging of Human Red Blood Xells Using TOF-SIMS," In: G. Gillen, R. Lareau, J. Bennett, F. Stevie, (Eds.), *Secondary Ion Mass Spectrometry (SIMS XI)*. John Wiley and Sons, New York, 1998, p. 93.
4. C. Fenselau, "MALDI MS and Strategies for Protein Analysis," *Anal. Chem.*, Vol. 69, 1997, pp. 661A–665A.
5. E. R. Williams, "Tandem FTMS of Large Biomolecules," *Anal. Chem.*, Vol. 70, 1998, pp. 179A–185A.
6. P. G. Rouxhet, M. J. Genet, "Chemical Composition of the Microbial Cell Surface by X-ray Photoelectron Spectroscopy," in: Mozes, N., Handley, P. S., Busscher, H. J., Rouxhet, P. G. (Eds.), *Microbial Cell Surface Analysis Structural and Physicochemical Methods*, VCH Publishers, New York, 1991, p. 175.
7. F. Caccavo, Jr., P. C. Schamberger, K. Keiding, P. H. Nielsen, "Role of hydrophobicity in adhesion of the dissimilatory Fe(III)-reducing bacterium *Shewanella alga* to amorphous Fe(III) oxide," *Appl. Environ. Microbiol.*, Vol. 63, 1997, pp. 3837–3843.
8. D. Briggs, M. P. Seah, "Practical Surface Analysis, Volume 1—Auger and X-ray Photoelectron Spectroscopy," *J. Wiley*, 1990, Chichester, England, p. 437.
9. H. Y. N. Holman, D. L. Perry, J. C. Hunter-Cevera, "Surface-Enhanced Infrared Absorption-Reflectance (SEIRA) Microspectroscopy for Bacteria Localization on Geologic Material Surfaces," *J. Microbiol. Methods*, Vol. 34, 1998, pp. 59–71.
10. J. C. Vickerman, "The SIMS phenomenon—the experimental parameters," In: Vickerman, J. C., Brown, A., Reed, N. M. (Eds.), *Secondary Ion Mass Spectrometry Principles and Applications*, Oxford Science Publications, New York, 1989, p. 31.
11. G. S. Groenewold, A. D. Appelhans, G. L. Gresham, J. E. Olson, M. Jeffery, J. B. Wright, "Analysis of VX On Soil Particles Using ion Trap Secondary Ion Mass Spectrometry," *Anal. Chem.*, Vol. 71, 1999, pp. 2318–2323.
12. M. L. Pacholski, D. M. Cannon, Jr., A. G. Ewing, N. Winograd, "Imaging of Exposed Headgroups and Tailgroups of Phospholipid Membranes by Mass Spectrometry," *J. Am. Chem. Soc.*, Vol. 121, 1999, pp. 4716–4717.
13. J. M. McMahon, R. T. Short, C. A. McCandlish, J. T. Brenna, P. J. Todd, "Identification and Mapping of Phosphocholine in Animal Tissue by Static Secondary Ion Mass Spectrometry and Tandem Mass Spectrometry," *Rapid Commun. Mass Spectrom.*, Vol. 10, 1996, pp. 335–340.

14. J. E. Delmore, A. D. Appelhans, E. S. Peterson, "Tube Ion Source for the Study of Chemical Effects In Surface Ionization," *Int. J. Mass Spectrom. Ion Proc.*, Vol. 108, 1991, pp. 179–87.
15. J. E. Delmore, A. D. Appelhans, E. S. Peterson, "A Rare Earth Oxide Matrix for Emitting Perrhenate Anions," *Int. J. Mass Spectrom. Ion Proc.*, Vol. 146/147, 1995, pp. 15–20.
16. G. S. Groenewold, J. E. Delmore, J. E. Olson, A. D. Appelhans, J. C. Ingram, D. A. Dahl, "Secondary Ion Mass Spectrometry of Sodium Nitrate: Comparison of ReO_4^- and Cs^+ Primary Ions," *Int. J. Mass Spectrom Ion Proc.*, Vol. 163, 1997, pp. 185–95.
17. K. Poels, L. Van Vaeck, R. Gijbels, "Microprobe Speciation Analysis of Inorganic Solids by Fourier Transform Laser Mass Spectrometry," *Anal. Chem.*, Vol. 70, 1998, pp. 504–512.
18. A. D. Appelhans, J. E. Delmore, "A Comparison of Polyatomic and Atomic Primary Beams for Secondary Ion Mass Spectrometry of Organics," *Anal. Chem.*, Vol. 61, 1989, pp. 1087–93.
19. P. C. Schamberger, F. Caccavo, Jr., F. V. O. Kloeke, G. G. Geesey, "Microbial Cell Fingerprinting – Development of TOF-SIMS for the Study of Microbial Cell Surfaces," *Abstract for Surfaces in Biomaterials Conference, Phoenix, AZ, 1996*.
20. A. D. Appelhans, D. A. Dahl, J. E. Delmore, "Neutralization of Sample Charging in Secondary Ion Mass Spectrometry Via a Pulsed Extraction Field," *Anal. Chem.*, Vol. 62, 1990, pp. 1679–1686.
21. J. C. Vickerman, "Introducing Secondary Ion Mass Spectrometry" In: *Vickerman, J. C., Brown, A., Reed, N. M. (Eds.), Secondary Ion Mass Spectrometry Principles and Applications*, Oxford Science Publications, New York, 1989, p.1.
22. D. A. Dahl and A. D. Appelhans, "Sample Charge Compensation Via Self-Charge-Stabilizing Ion Optics," *Int. J. Mass Spectrom. Ion Proc.* 178, 1998, pp. 187–204.
23. G. S. Groenewold, A. D. Appelhans, J. C. Ingram, "Characterization of Bis(alkylamine)mercury Cations from Mercury Nitrate Surfaces By Using an Ion Trap Secondary Ion Mass Spectrometer," *J. Am. Soc. Mass Spectrom.* 9, 1998, pp. 35–41.
24. S. D. Brown, "Chemical Systems Under Indirect Observation: Latent Properties and Chemometrics," *Appl. Spectrosc.* 49, 1995, pp. 14A–31A.
25. D. M. Haaland, R. G. Easterling, D. A. Vopicka, "Multivariate Least-Squares Methods Applied to Quantitative Spectral Analysis of Multicomponent Samples," *Appl. Spectrosc.*, Vol. 39, 1985, pp. 73–84.
26. D. M. Haaland, E. V. Thomas, "Partial Least-Squares Methods for Spectral Analysis. 1. Relation to Other Quantitative Calibration Methods and Extraction of Qualitative Information," *Anal. Chem.*, Vol. 60, 1988, pp. 1193–1201.
27. T. Naes, H. Martens, "Principal Component Regression In NIR analysis: Viewpoints, Background Details and Selection of Components," *J. Chemom.*, Vol. 2, 1988, pp. 155–67.
28. L. Dolmatova, C. Ruckebusch, N. Dupuy, J. P. Huvenne, P. Legrand, "Quantitative Analysis of Paper Coatings Using Artificial Neural Networks," *Chemom. Intel. Lab. Syst.*, Vol. 36, 1997, pp. 125–40.

29. F. Basile, M. B. Beverly, C. Abbas-Hawks, C. D. Mowry, K. J. Voorhees, T. L. Hadfield, "Direct Mass Spectrometric Analysis of in situ Thermally Hydrolyzed and Methylated Lipids From Whole Bacterial Cells," *Anal. Chem.*, Vol. 70, 1998, pp. 1555–1562.
30. S. A. Barshick, D. A. Wolf, A. A. Vass, "Differentiation of Microorganisms Based on Pyrolysis-Ion Trap Mass Spectrometry Using Chemical Ionization," *Anal. Chem.*, Vol. 71, 1999, pp. 633–641.

Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface

Refining Baseline Tracer Levels for Groundwater Modeling

Travis L. McLing (INEEL); DeWayne Cecil (USGS);
Vladimir B. Aizen (University of Santa Barbara, CA)

SUMMARY

EM is charged with establishing radionuclide inputs to the environment from facilities within the DOE complex. In some cases, disposal of radionuclide bearing waste at the INEEL has resulted in large diffuse groundwater contamination plumes. INEEL stewardship requires that scientists understand the fate and transport issues dealing with such plumes in the Snake River Plain aquifer. Radioactive chlorine (^{36}Cl), a constituent in the plume at the Idaho Nuclear Technology and Engineering Center (INTEC) on the INEEL, has the potential to be an ideal tracer to define the extent that contamination has spread from the point source. To use ^{36}Cl in this manner, all its potential sources (weapons tests, in situ production, disposals, and natural background) must be fully characterized. Data for long-term background and weapons tests are the most difficult parameters to obtain. For example, precipitation records (one important source of information) have not been kept for the last 50 to 60 years; however, the isotopic record locked up in glacial ice provides a region-specific record of the weapons-tests inputs and background values for cosmogenic isotopes prior to the weapons test of the 1950 and 1960s. Therefore, mid-latitude glacial ice needs to be collected and analyzed to determine long-term background and weapons test input baselines. The research funded in this work package on mid-latitude glaciers will significantly enhance our understanding of the inputs of Pu isotopes, and ^{14}C , ^3H , and ^{36}Cl to the environment. In this context, it will aid in delineating multiple sources worldwide such that the contributions from EM operations can be better characterized.

This research has permitted the quantification of preanthropogenic background concentrations of several radioactive constituents, including ^{36}Cl , the primary focus of this study. This radioactive nuclide is being used to better define aquifer characteristics including flow velocity, dispersivity, and attenuation for use in flow and transport models at contaminated sites within the DOE complex. ^{36}Cl concentrations in mid-latitude glacier ice cores have allowed researchers to further define the preweapons test and weapons test (non-INEEL source) inputs to the hydrosphere for this radionuclide. Additionally, increased precision in calibration of groundwater modeling in the Snakeriver Plain aquifer will result in unprecedented resolution for flow and transport models at DOE sites.

TASK DESCRIPTION

Groundwater modeling is a key component of EM characterization and remediation activities at the INEEL and throughout the DOE complex. However, models must be validated (compared against measurements) and calibrated (fit to measurements by refining input parameter values) to be valid and useful. Because we are using cosmogenic isotopes, multiple background sources must be subtracted from concentrations in the aquifer. Clearly, this requires that nonsource inputs (natural background and bomb input) be identified and subtracted at any given point in the aquifer. Subtracting background is especially difficult at the leading-edge of a plume where source to background ratio is very low and modeling results are most critical. Currently these background numbers suffer from a high degree of error associated with

the lack of accurate atmospheric inputs. Our previous research interrogated the only source of cosmogenic isotope data for the 1950s and 60s in North America. To support the data collected in 1998 we will study several mid-latitude glacial sites in Central Asia. This new information will be used to test the new model for groundwater flow and transport in and near the INEEL.

^{36}Cl is of particular interest to this task because:

- It is found in a contaminant plume originating from INTEC
- It occurs in virtually all natural systems as an anion (because of its high electron affinity) resulting in minimal chemical interaction
- Chloride is also extremely hydrophilic making it an especially good hydrologic tracer
- It has long half-life (3×10^5 -y), eliminating decay concerns
- AMS detects ^{36}Cl at extremely low levels.

There are however, difficulties with using ^{36}Cl as a tracer; the following information is needed to fully use this methodology:

- The global preanthropogenic background must be well characterized
- Atmospheric weapons test input (1950–1960s) must be well characterized
- Regional transport/deposition properties for the Eastern Snake River Plain need to be better characterized.
- Inputs from sources other than the INTEC deep injection well must be characterized, and the resulting background concentration in the aquifer must be accurately determined
- Input concentration for injected water at INTEC needs to be known.

The isotope is produced naturally by neutron activation of ^{35}Cl in the upper atmosphere. The largest historical input of ^{36}Cl to the hydrosphere is from atomic weapons testing in the 1950s and 60s. This record of events is now preserved in glacier ice. Because of mid-latitude atmospheric global circulation patterns, it is highly desirable to obtain ice core isotopic data from glaciers located at mid-latitudes. There are a limited number of glaciers at these temperate latitudes that are at a high enough elevation to not experience melt water percolation which will “smear” the isotopic record through deeper ice core layers making the concentration measurement meaningless. The Upper Fremont Glacier (UFG) in the Wind River Range of Wyoming, 260 km east of the INEEL and the Inilchek Glacier in the Kyrgyz Republic in Central Asia meet this specific criteria.

^{36}Cl concentrations have been measured in an ice core from the UFG—providing the only data available for determining regional ^{36}Cl background input. The validity of using UFG data to represent the ^{36}Cl background at the INEEL needs to be confirmed by data collected from another site. Consequently, ice core will be collected from the Inilchek Glacier. It is expected that this data collected from this new site will support the data collected at the UFG providing an applicable data set for other mid-latitude aquifers including that of the Eastern Snake River Plain.

A small portion of the ESRC funding requested in this work package will contribute in part to an U.S. Geological Survey (USGS) ice coring effort this summer on the Inilchek Glacier. The remainder of the ESRC Program funding requested in this work package will be used to support a ^{36}Cl and other isotope research components which will provide the requisite data to validate and substantiate the UFG ^{36}Cl data. Ice coring at the Inilchek Glacier will largely be funded by National Science Foundation and USGS to support a global climate change research component, the cost sharing for this study means that an invaluable amount of data will be collected and reduced at an exceedingly low cost. Additionally, a portion of the work described will support the completion of a snow survey that is being conducted on the UFG to determine the fraction of ^{36}Cl lost to ablation and or melt-water. Knowledge of this lost ^{36}Cl is critical in the determination of true atmospheric input of atmospheric ^{36}Cl inputs to the Snake River Plain aquifer.

ACCOMPLISHMENTS

Mid-latitude sites visited in FY 2000 included the UFG, Inilchek Glacier, and Yulong Glacier (in Southern China, People's Republic of China (PRC)).

Expeditions to the Yulong Glacier, Inilchek Glacier, and UFG were conducted in FY 2000. The expedition to the PRC was at the invitation of the Chinese Academy of Sciences (CAS) and the Lanzhou Glacial Institute to perform joint glacial studies with the USGS and with Dr. Vladimir B. Aizen at the University of California Santa Barbara (UCSB). The purpose of the April 2000 reconnaissance expedition into the Yulong Glacier was to determine if ice-core drilling and research at this site would be beneficial to the UCSB, the USGS, and our Chinese collaborators. Studying this and other glaciers in China is planned for the future through cooperative agreements with Chinese institutions and scientists. After leaving China and before returning to the U.S., DeWayne Cecil and Dr. Aizen were invited to give lectures in Japan at their glaciological research institute in Tokyo. The topic of these lectures was worldwide mid-latitude glacier research being conducted by the UCSB and the USGS.

An expedition to the Inilchek Glacier in the Tien Shan Mountains, Kyrgyzstan, Central Asia, was undertaken in FY 2000 by an international team of 18 scientists from six countries. Two deep ice cores were drilled during this time to total depths of 162 m and 167 m. Additionally, 100 m of core was collected for radioisotope analysis. Snowpit samples spanning the entire elevation range of the glacier, as well as fresh snowfall events were also collected. A GPS survey of a network of stakes positioned on the glacier was conducted at the beginning and ending of the expedition to determine surface velocity of the glacier and to aid in modeling glacier flow. Temperature measurements of the first borehole showed that the temperature of the glacier was -11.3°C at 160 m below the surface, indicating that the glacier is frozen to bedrock. A radio-echo sounding survey was completed with over 150 locations measured across the surface of the glacier. A borehole gamma spectrometer was used to log radioactivity in the upper 30 m of the first borehole. An automated weather station collected meteorological data during the 2-month expedition.

One expedition to the UFG to service meteorological and depth-sensor stations was accomplished in FY 2000. This task is a continuation of fieldwork at the UFG site started by the USGS in 1987.

A number of articles, a report, a USGS fact sheet, and numerous abstracts were published (see Appendix A) or are in the process of being prepared and submitted. DeWayne Cecil signed a contract with Kluwer Academic Publishers to serve as senior editor.

Several invited ice-core task briefings were presented to researchers and personnel from Universities, the State of Idaho, National Laboratories, DOE Headquarters, and USGS (see Appendix A).

REFERENCES

None

Subsurface Understanding

This area of research deals with the subsurface environment. The characterization and control of this complex domain is vital to successful environmental management. The research here encompasses a broad range of activities involving the sciences of biology, chemistry, physics, hydrology, and geology. Furthermore, the physical scale of measurement is vast, extending from microns to kilometers. Our overall success in meeting our EM goals will depend in large part on our ability to understand and control contaminants within the earth's surface.

The following tasks are reported in this section:

- Geological, Geophysical, and Hydrological Environs of the INEEL Site
- Complex Systems Theory Applied to Subsurface Transport
- Ecological Engineering of Rhizosphere Systems
- Investigation of Factors Influencing Cesium Mobility and Uptake In Plant/Soil Systems
- Long-Term Biogeochemical Destruction and Control of Aquifer Contaminants Using Single-Well Push-Pull Tests
- Unified Hydrogeophysical Parameter Estimation Approach to Subsurface Contaminant Transport—Subsurface Imaging Collaboration with the Center for Subsurface Sensing and Imaging Systems
- Innovative Approaches to Characterize Vadose Zone Hydraulic Properties.

Geological, Geophysical, and Hydrological Environs of the INEEL Site

Refining our Understanding of INEEL Groundwater Flow

Richard P. Smith (INEEL); Paul Link, Glenn Thackray, Joe Kruger, Rick Allison, and Andy Smith (ISU); Glen Embree and Kathleen Price (BYU Idaho/Ricks); Bill Bonnicksen, Martha Godchaux, and John Welhan (Idaho Geological Survey/University of Idaho)

SUMMARY

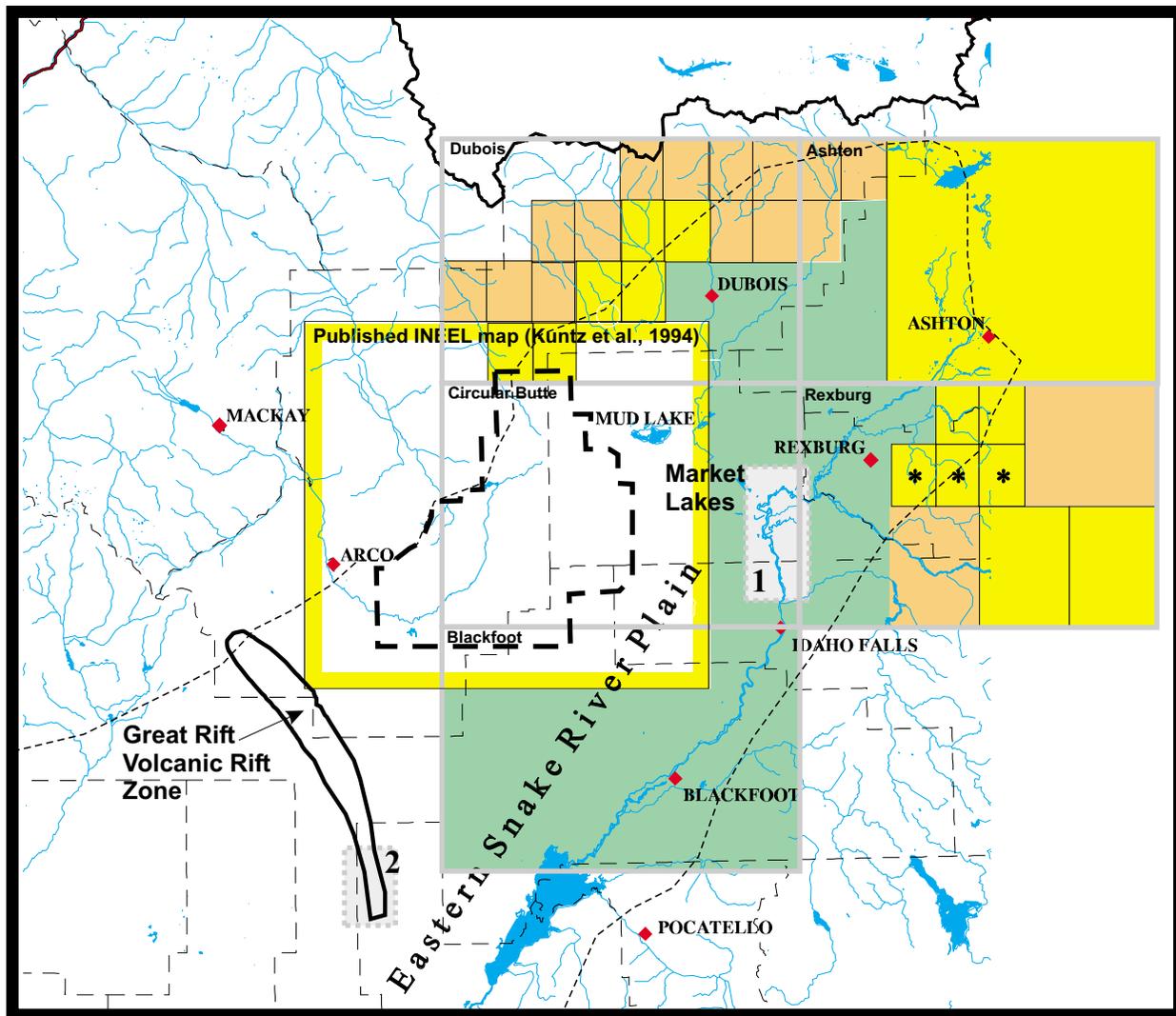
Scientifically defensible decisions about disposal, cleanup, and stewardship alternatives require that INEEL-specific sites be understood in the context of regional geologic and hydrologic processes and subsurface environments. Existing data shows that groundwater flow directions in the aquifer are strongly influenced by the regional stress field in the earth's crust, variations in aquifer thickness, input of geothermal waters from depth, preferred orientations of sediment interbeds and lava flows, and fractures and dikes in volcanic rift zones. All of these factors produce an anisotropy (bias) in hydraulic conductivity that makes groundwater flow in directions quite different from that indicated by the hydraulic gradient.

The purpose of this task is to facilitate better understanding of the subsurface regional context of the INEEL by (a) synthesizing existing unpublished information and compiling it into a common format so that all information is available and useful for decision making, and (b) performing several short-term field investigations that will complete the aerial coverage and provide a comprehensive understanding of regional geologic and hydrologic processes. The area selected for these activities includes a large portion of the Eastern Snake River Plain and adjacent mountains (Figure 1). This provides INEEL-specific geologic and hydrologic data in its proper regional context. Such regional understanding is necessary because up-gradient processes in the Snake River Plain aquifer affect the INEEL, INEEL activities and past practices affect down-gradient regions of the aquifer, and regional seismic and volcanic processes affect the current operation of facilities and long-term stewardship of waste disposal facilities at the INEEL.

This research focuses on developing a better understanding of all the factors that influence aquifer dynamics and geometry. The results will improve our assessments of contaminant transport in the aquifer and furnish boundary conditions for detailed modeling of INEEL-specific sites.

The large body of unpublished geoscience information that exists for the region (geologic mapping, geophysical surveys, and volcanic processes investigations) is being compiled digitally in the geographical information system (GIS) format on 1:100,000-scale maps so that it adjoins seamlessly with the current geologic map of the INEEL (see Figure 1).¹ This year, GIS personnel were hired at Idaho State University (ISU) and trained at the Idaho Geological Survey (IGS) electronic map publication office, and three of the 7.5 minute quadrangles of the Rexburg 1:100,000-scale sheet were completed and sent to IGS for publication.

Several field investigations were started this year (see Figure 1). Field mapping of the Snake River corridor north of Idaho Falls, the rhyolitic volcanic rocks along the north margin of the Eastern Snake River Plain, and several quadrangles northwest of Rexburg will fill the biggest areas where very little geologic data exists. Detailed geophysical data for an area in the southern Great Rift were collected in order to test the ability of magnetic and gravity surveys to detect dikes in the subsurface.



Gc00 0699

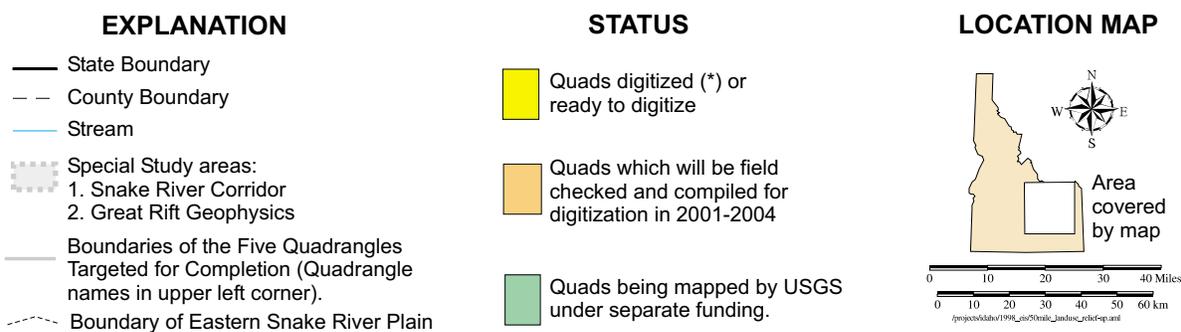


Figure 1. Regional map showing stream drainages, major towns, locations of the five 1:100,000-scale quadrangles to be completed in this task, locations of special study areas, and status of geologic mapping.

TASK DESCRIPTION

This is a broad integration and synthesis task. It employs the expertise of geoscientists with specific knowledge of various aspects of Eastern Snake River Plain geology, and takes advantage of a large body of unpublished geologic mapping that is relevant to regional aquifer problems in the INEEL area. The unpublished information includes:

- Mapping by the United States Geological Survey (USGS)
- Mapping by geologists at ISU and BYU Idaho
- Geophysical surveys performed by INEEL programs
- Geophysical surveys performed by other institutions
- State-of-the-art knowledge of volcanic processes operating during the origin of the Eastern Snake River Plain by IGS personnel
- Several short-comings of the existing database, in terms of both unstudied areas near the INEEL and gaps in geologic understanding, are being addressed by relatively inexpensive, short-term field investigations. The purpose of this task is to synthesize the existing information and to compile it into a common format so that all information is available and useful for decision making, and perform several short-term field investigations that will complete the aerial coverage and provide a comprehensive understanding of regional geologic and hydrologic processes.

This task is divided into the following subtasks, each with a focused objective and overarching synthesis that incorporates the results from each activity into the development of improved conceptual models of INEEL-area geology and hydrology:

1. *Define the geomorphology and geology of the Snake River corridor north of Idaho Falls (Figure 1, Special Study Area 1).* This is a focus because very little information exists for the area and the Snake River in this region exhibits aggradation features (suggesting crustal subsidence) and a lack of terraces typical of down-cutting rivers. Therefore, this task fills in an area of unknown geology on the map and addresses a lack of conceptual understanding of riverine processes in the area.
2. *Perform microgravity and magnetic surveys of known dike systems in the Great Rift volcanic rift zone (see Figure 1, Special Study Area 2).* This is the field acquisition part of the assessment of geophysical techniques to identify subsurface dikes that affect aquifer flow. The field acquisition phase includes the collection of raw microgravity and magnetic data across known dikes. Complete data reduction and processing to interpret the relationships of gravity and magnetic anomalies to dike positions and depth beneath the surface will occur in the following years.
3. *Compile and field verify existing geologic mapping in the Rexburg quadrangle (see Figure 1, status blocks for Rexburg quadrangle).* This task takes advantage of several decades of geologic mapping by Glenn Embree and Roger Hoggan and their students at BYU Idaho. Much of the work was supported by the USGS in their Snake River Plain research project in the 1970s, some was supported by INEEL for seismic hazards assessment in the 1990s, and some was supported by field activities at BYU Idaho. Several 7.5 minute quadrangles are completed or nearly completed. This task comprises field verification and compilation of existing maps and development of plans for additional study of unmapped

areas in follow-on years. As the maps are compiled and field checked, they will be sent to the GIS laboratory at ISU for digitization.

4. *Evaluate rhyolites and calderas beneath the INEEL area.* Rhyolitic volcanic rocks which erupted from calderas beneath the INEEL area are exposed along the north margin of the Snake River Plain in the Dubois and western part of the Ashton quadrangles (see Figure 1, status blocks for the Dubois and Ashton quads). These rocks contain information about the eruption mechanisms, caldera locations, and magmatic processes in the early evolution of the Eastern Snake River Plain, but they have not been studied in the detail necessary to yield that information. Geologists from the Idaho Geological Survey, who are recognized experts on similar rock sequences in the Western Snake River Plain, are applying their expertise to evaluate the rocks in this area.
5. *Produce digital geologic maps so the spatial geologic information acquired in this task will be of maximum value for modeling of the subsurface physical environment.* The information will be digitized by the GIS laboratory at the ISU Geology Department. This will allow analysis of the information with hydrologic and contaminant data already existing in GIS format. The task involves training an ISU GIS technician to the state-of-the-art in digital map preparation at the Idaho Geological Survey GIS laboratory and digitization of compiled maps as they are completed. Digitized maps will be published by the IGS, which has developed and maintains a national leadership role in digital geologic map publication.
6. *Conduct geoscience workshops.* A field workshop held towards the end of the fiscal year will allow the participants to actively interact and learn from each other's discoveries. The participants will present the results of the first year's work and develop plans for the following year. After this first year, workshops will be held twice a year, once in spring to discuss data analysis completed during the previous winter and to plan the summer's activities, and once in the fall, to summarize the year's work, discuss field results, and plan work for the following year.
7. *Synthesize task results.* The results of the specific tasks are likely to provide maximum benefit to INEEL conceptual models only if they are interpreted in relationship to each other and to existing conceptual models. The synthesis task is designed to assure that we reap maximum benefit by examining all the implications of specific task results to regional processes that affect the aquifer and subsurface environment beneath the INEEL area.

ACCOMPLISHMENTS

The major accomplishments for FY 2000, summarized below, are keyed by number to the tasks introduced in the Task Summary section, above.

1. In FY 2000, aerial photograph and topographic map interpretation of flood plain and sediment landform features along the Snake River between Idaho Falls and Menan (see Figure 1, Special Study Area 1), field investigations (descriptions, sampling, relative age assessments, stratigraphic sequence determinations), and a preliminary map of surficial deposits along the river were completed. In addition four boreholes were drilled in the area to examine stratigraphic relationships and to obtain samples for age determinations. The work shows that the area has been the site of a lake during much of recent geologic time (Market Lake is a remnant), that the river's course has been affected by basaltic volcanism, and that river terraces characteristic of down-cutting rivers are absent north of Idaho Falls but present between Idaho Falls and Blackfoot. Instead of characteristic terraces, the South

Fork has built a large alluvial fan that forces the river westward against basalt lava flows. The absence of terraces appears to be partly due to intensive farming activities in the area, but the fact that farming practices can destroy geomorphic evidence of terraces indicates that any original terraces were very small. This corroborates first-order leveling data^{2,3} that reveal rapid crustal subsidence in the Snake River Plain north of Idaho Falls, and suggests a long duration for the subsidence, extending back into Pleistocene time. This is independent evidence for differential crustal subsidence in the Eastern Snake River Plain, a process suspected based on variations in basalt accumulation rates and stratigraphic correlation in INEEL area wells.⁴

2. Detailed geophysical data were collected along three lines across a known dike in the southern Great Rift, south of Craters of the Moon volcanic field (see Figure 1, Special Study Area 2). The goal of these surveys is to test the ability of detailed magnetic and gravity data to detect dikes or dike swarms in the subsurface. There is both a theoretical and observational basis for believing that magnetic and gravity data are sensitive to dikes of basalt cutting basalt lava flows^{5,6} and this is the first test in the Snake River Plain. Only the data collection step was completed this year, and the data processing and interpretation necessary to complete the test will be done in follow-on years. This is an important test because we know that many dikes exist in the subsurface of the INEEL area, and that their NW trending orientation is almost perpendicular to the regional direction of groundwater flow. They are likely to affect the direction and velocity of groundwater flow because of their much lower permeability than interlayered basalt lava flows, but we lack ways to detect their presence and geometry. This year's activity is the first step in assessing the viability of using geophysical techniques to detect locations and geometries of dikes that may influence aquifer flow.
3. Field verification and compilation of three 7.5-minute quadrangles in the Rexburg 30 × 60 ft sheet were completed, the compilation sheets were digitized at the ISU GIS laboratory, and the digital files are in review and preparation for publication at the IGS (see Figure 1, yellow status blocks with asterisks). Field verification of several more of the 7.5-minute quadrangles is complete and compilation during the winter months will provide more maps to be digitized at ISU (see Figure 1, orange status blocks in the Rexburg quad).
4. Reconnaissance examination of rhyolitic rocks along the northern margin of the Snake River Plain was completed in FY 2000. This included field checking of previous mapping in six 7.5-minute quadrangles and confirmation that all six are adequate and ready for digitization and publication (see Figure 1, yellow status blocks in Dubois and Ashton quads, and Figure 2). Fourteen quadrangles have incomplete mapping and field activities will be focused in them over the next 3 years (see Figure 1, orange status blocks in Dubois and Ashton quads). Five different domains of faulting were recognized in the area, each representing a different time period and a different style of tectonism. Investigations of the relationships among these domains during the next 3 years will clarify tectonic and volcanic relationships and improve seismic hazards assessments for the INEEL. Many flow-direction indicators were recognized in the rhyolitic rocks; they suggest that some of the rhyolitic units had multiple sources beneath the basalts of the Snake River Plain and that the calderas that fed them had a complex eruptive history.

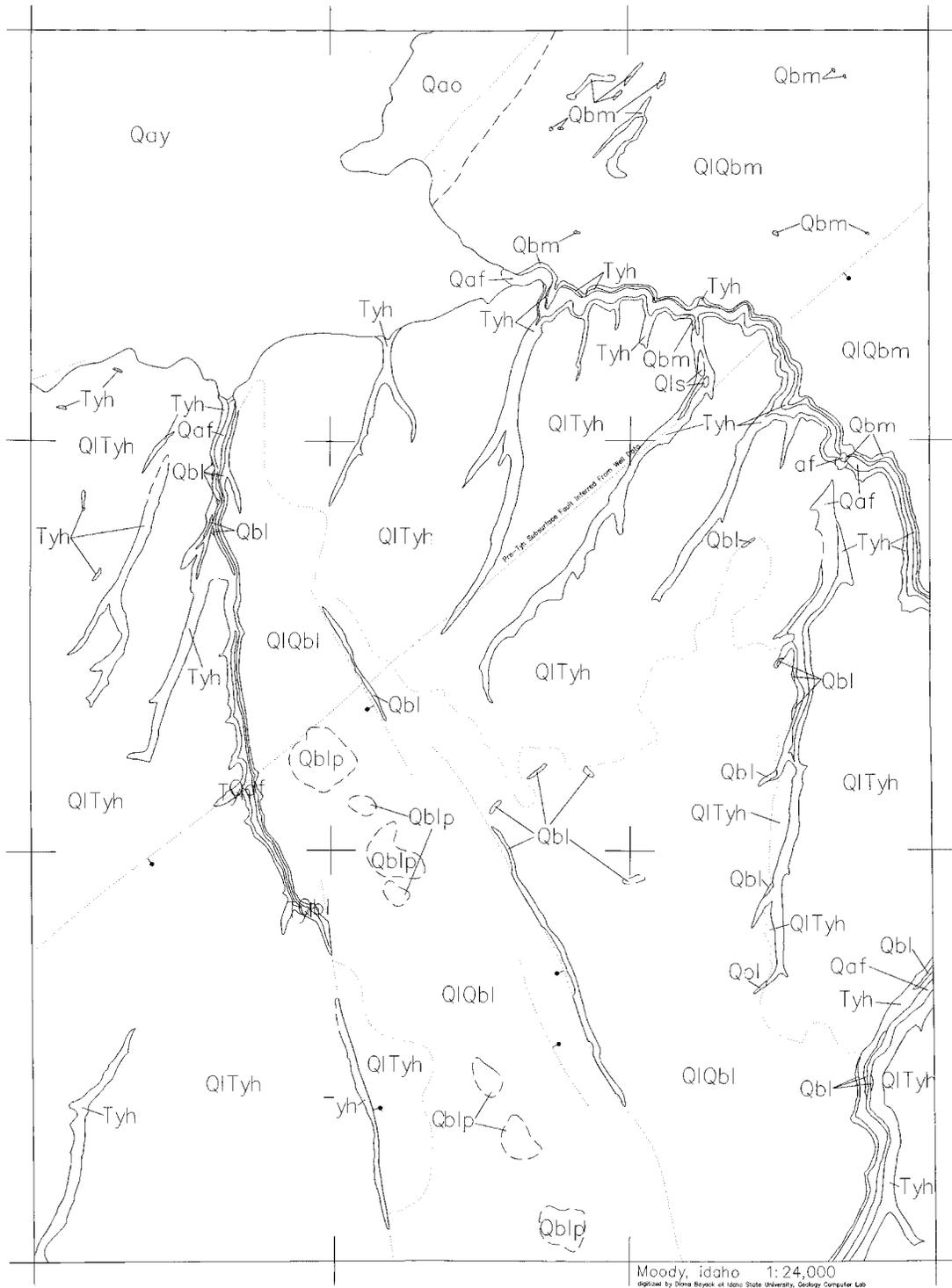


Figure 2. One of the completed digital geologic map files sent to IGS for publication. The outlined areas represent the outcrop areas of a different rock units and the letter designations are abbreviated identifiers for each rock type. The geologic information in the digital files will be presented in the final published maps as areas of different color overlain on topographic maps which show landforms, drainages, and political boundaries.

Additional work on these features will provide a better conceptual understanding of the volcanic structures and geothermal systems likely to be found beneath the basalts in the INEEL region. The interaction of geothermal systems with the Snake River Plain aquifer can potentially influence aquifer flow directions and velocities. Reconnaissance investigations completed this summer helped to develop a work plan for detailed investigations to be carried out in follow-on years.

5. Development, staffing, and training of GIS laboratory at ISU with capability to produce digital geologic map files in format compatible with Idaho Geological Survey map publication standards. Three 7.5 minute digital quadrangle maps were produced and sent to IGS for peer review and publication (see Figure 2). The ultimate publication of digital geologic maps of the entire region affecting the INEEL will provide the regional context of aquifer processes and valid boundary conditions for the INEEL aquifer flow and contaminant transport models. In early September 2000, the participants gathered in Idaho Falls for the first of several scheduled workshops. The 2-day workshop was a field-based examination of the areas where work has been done in FY 2000. It allowed participants to present the results of the first year's work, to receive feedback from the other researchers, and to develop plans for the following year. The synergy developed in this workshop was especially productive in the area along the Snake River north of Idaho Falls (see Figure 1, Special Study Area 1), where the lava flow eruption history and the accumulation history of river sediments were brought together for the first time. This provided ideas for testable hypotheses about crustal subsidence, river aggradation, the potential role of lava dams in development of lake sediments and river course migration, and the isolation of the Mud Lake basin (and INEEL area) from the Snake River drainage system. All of these processes have important implications for INEEL-area hydrology, and they seem to converge in the a single area of the Snake River drainage.
6. The synthesis of the results of the work on this task for the first year have confirmed our expectations that advances in regional understanding would appear, and that unforeseen relationships would come to light. After only about 6 months of work we have made the following important advances:
 - Independent evidence of differential crustal subsidence along the Snake River north of Idaho Falls provides more confidence in interpretations that differential subsidence occurs in the crust beneath the INEEL. This is important to aquifer understanding because differential subsidence rates can help to explain variations in aquifer thickness across the INEEL and help us to better predict the areas where the aquifer is unusually thick or thin. It is also important from a seismic and volcanic hazards point of view because it provides a better picture of regions where faulting and volcanism are concentrated.
 - The discovery of spatially and temporally different faulting domains along the northern margin of the Snake River Plain will improve seismic hazards assessments at the INEEL by giving us a better picture of the mechanisms and rates of crustal subsidence of the Snake River Plain, and of the interaction of the subsidence process with faulting related to regional basin-and-range extension in the mountains adjoining the Snake River Plain.

- Our best hope of improved understanding of rhyolitic volcanic processes that operated in the Snake River Plain before the accumulation of the basaltic lava flows is by detailed investigations of the erupted rhyolites that are still preserved in the valleys north of the Snake River Plain. The discovery that there were multiple source areas for one of these rhyolite units provides a clearer picture of the geometry of calderas underlying the basalts on the Snake River Plain. This is important because caldera geometry is one of the major controls of the locations of deep-seated geothermal systems that impinge on the base of the aquifer and affect its chemistry, temperature, and flow dynamics.
- We collected an extensive geophysical data set, consisting of gravity and magnetic data at thousands of stations across known dike systems. This will allow assessment of the viability of geophysical detection of unknown dikes. Knowledge of the locations and geometries of dikes in the subsurface will help to understand aquifer flow and provide better seismic and volcanic hazards assessments.

REFERENCES

1. M. A. Kuntz, et. al., “Geologic map of the Idaho National Engineering Laboratory and Adjoining Areas, Eastern Idaho,” *U.S. Geological Survey Miscellaneous Investigation Map, I-2330*, 1:100,000 scale, 1994.
2. J. R. Pelton, *Analysis of Geodetic Leveling Data in the Vicinity of the INEL*, EG&G, Informal Report EGG-NPR-10691, 48 p. plus appendices, 1991.
3. R. E. Reilinger, G. P. Citron, and L. D. Brown. 1977, “Recent Vertical Crustal Movements from Precise Leveling Data in Southwest Montana, Western Yellowstone National Park, and the Snake River Plain,” *Journal of Geophysical Research*, Vol. 82, No. 33, 1977, p. 5349–5359.
4. S. R. Anderson, M. J Liszewski, and L. D. Cecil, “Geologic Ages and Accumulation Rates of Basalt-flow Groups and Sedimentary Interbeds in Selected Wells at the Idaho National Engineering Laboratory, Idaho,” DOE/ID-22134, *U.S. Geological Survey Water Resources Investigations Report*, 97-4010, 1997.
5. V. J. Flanigan and C. L. Long, 1987, “Aeromagnetic and Near-surface Electrical Expression of Kilauea and Mauna Loa Volcanic Rift Systems”, in *Volcanism in Hawaii*, *U.S. Geological Survey Professional Paper 1350*, R. W. Decker, T. L. Wright, and P. H Stauffer, editors, 1987, pp. 935–946.
6. G. Schoenharting and G. Palmason , “A Gravity Survey of the Reydarfjordur Area, Eastern Iceland, with Interpretation” *Journal of Geophysical Research*, Vol. 87, 1982, pp. 6419–6422.

Complex Systems Theory Applied to Subsurface Transport

Exploring the Complexity of How Contaminants Move Through the Ground

Thomas Wood, Daphne Stoner, Charles Tolle, Randall LaViolette, John James (INEEL); John Crepeau (ISU); Boris Faybishenko (LBNL); David Peak (USU)

SUMMARY

The capability to predict the transport of radionuclides, chlorinated hydrocarbons, and other pollutants in the subsurface has become one of the most important challenges facing DOE. Research in vadose zone flow and transport is continually revealing that the vadose zone is a complex environment. Computer modeling of the vadose zone and contaminant monitoring strategies are paramount to long-term remedial actions required to meet DOE stewardship commitments, as well as to understanding contaminant fate and transport for more immediate EM remediation activities. Many computer simulations rely on simplified flow and transport models. Existing subsurface computer models are inaccurate because they do not adequately factor in the dynamics of complex systems.

Example after example can be cited where within months to a few years of completion vadose zone fate and transport models require updating and recalibration based on new monitoring data. This constant reworking occurs despite the fact that the models purport to determine risk hundreds to thousands of years in the future.

Computer models that incorporate the complex interactions of geological, hydrological, chemical, and biological parameters will more accurately reflect the complexity of the real world. To make significant improvements in transport predictions, the complex and chaotic behavior of the real world must be incorporated into computer models. Incorporating nonequilibrium transport processes into numerical predictions and monitoring strategies will improve models required to meet long-term DOE stewardship commitments. Our long-term goal is to develop new algorithms for predicting flow and transport based on chaos theory or on a solution from complex systems theory (cellular automata, artificial neural networks, etc.). By doing so, we will advance the understanding of fundamental multiscale processes.

We conducted research under five subtasks. (Subtask 1) When comparing several vadose zone transport models to analyze monitoring data, we found that the data suggest a common emergent property for vadose zone transport may be that small volumes of relatively high concentrations (compared to center-of-mass calculations) of contaminants travel faster routes. (Subtask 2) A series of small-scale (1-meter) ponded infiltration tests conducted over a fractured basalt ledge in the Hell's Half Acre (HHA) lava field during 1998 and 1999 show highly variable flow rates, unrelated to the water head in the infiltration pond. We evaluated the data set for the existence of chaos and found we could not determine whether the system was chaotic because of problems associated with an integrate-and-fire data set. (Subtask 3) We evaluated a numerical tool for screening time series data sets for nonlinear behavior. The results are promising for application to environmental problems. (Subtask 4) We developed an approach for building a theoretical model of the Hell's Half Acre experiment that will capture the dynamical behavior of the system without the inherent problems of short, noisy data sets. (Subtask 5) We performed the first two steps for determining whether the governing equations of vadose zone flow and transport, which relate in nonlinear fashion, will act to generate chaotic dynamics. Work continues on this task, and we believe that our final results will improve how conceptual models are created for vadose zone transport by demonstrating that deterministic models overlook critical aspects of dynamic behavior.

TASK DESCRIPTION

Greater reliability of predictive modeling can be achieved by developing conceptual models that incorporate the complex interactions of geological, hydrological, chemical, and biological parameters arising from their nonlinear and nonadditive interactions. Incorporating nonequilibrium transport processes into monitoring strategies will improve data interpretation and improve system performance required to meet long-term DOE stewardship commitments. Many existing deterministic^a and stochastic^b subsurface models appear unreliable because they do not include the dynamics of complex systems.^c To make significant improvements in contaminant transport predictions, the onset and occurrence of chaotic^d and or complex behavior must be incorporated into the models. The detection of a few low-concentration contaminants in groundwater outside DOE waste sites can likely be explained by incorporating complex systems theory into predictive transport codes.

Developing scientifically sound, coupled experimental, theoretical, and or mathematical arguments to describe the impacts of complex system behavior on contaminant fate and transport movement will help DOE alleviate stakeholder concern over the apparent mismatch of occasional detection of contaminants outside zones predicted with traditional center-of-mass transport models. It supports several major initiatives for understanding and predicting contaminant fate and transport in complex subsurface environments and for applying this understanding to long-term stewardship of DOE legacy waste.^{1,2}

The task has two major objectives:

1. Explore application of innovative approaches that are not limited to idealized and simplified situations but that reflect real-world complexity.
2. Demonstrate a proof of concept that alternative approaches may be more appropriate than traditional methods of data analysis for vadose zone transport. This will be demonstrated by testing the validity of a complex systems theories approach, in this case deterministic chaos, on an INEEL data set.

To address these two objectives, we established five major subtasks for this task, one observational, two numerical, and two theoretical. These multidisciplinary subtasks are briefly summarized below.

Subtask 1. Looking for Complexity in Real Vadose Zones

The purpose of this subtask was to look at several transport simulations through vadose zones and compare them to monitoring data. Our intent was to qualitatively assess whether emergent patterns generally exist in vadose zone transport. We considered DOE waste disposal sites at the INEEL, Hanford Reservation, Yucca Mountain, and Nevada Test Site. Transport through the vadose zone to the groundwater at these sites has been shown not to follow predictive models. Our cursory review suggests that

a. Determinism is the philosophical belief that every event or action is the inevitable result of preceding events and actions. Thus, in principle at least, every event or action can be completely predicted in advance, or in retrospect if the starting points are exactly known.

b. Relating to, or governed by, probability. The behavior of a probabilistic system cannot be predicted exactly, but the probability of certain behaviors is known.

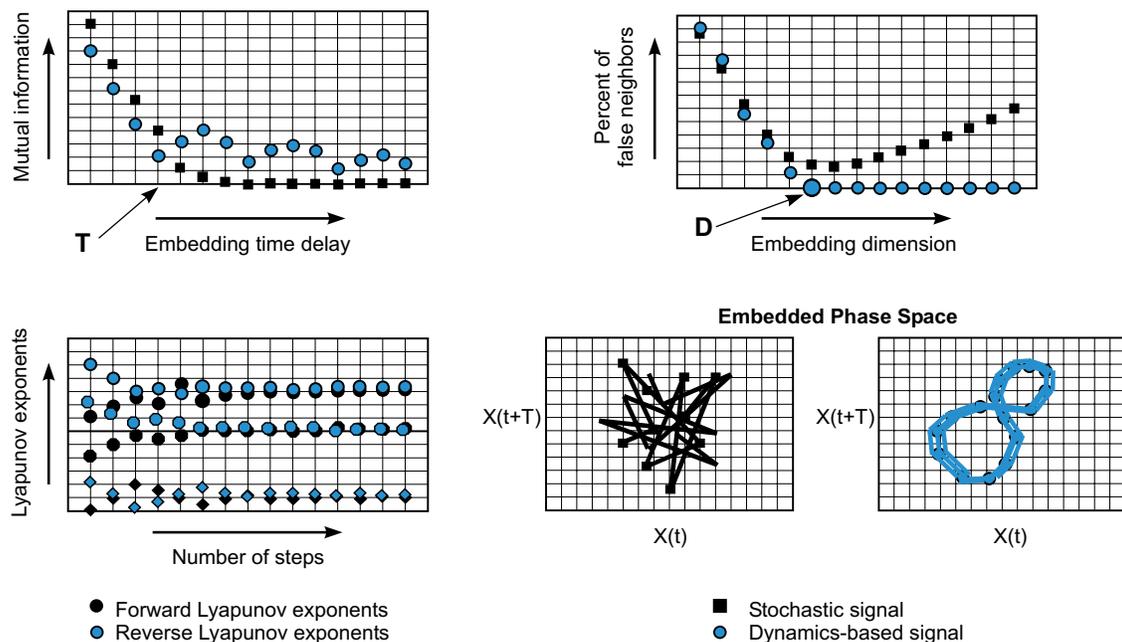
c. A complex system is a collection of many simple nonlinear units that operate in parallel and interact locally with each other so as to produce emergent behavior.

d. Chaos implies the ability to predict, at least for a few time steps, the system behavior based on previous system responses.

Subtask 2. Chaotic Analysis of the Hell's Half Acre Data Set

The goal of this numerical analysis subtask was to apply traditional chaotic procedures achieve better understanding of the underlining dynamics of flow through a fractured basalt vadose zone. This subtask was designed to reconstruct the phase-space attractor dynamics of the system based on observed droplet events. Many of these techniques are rooted in Taken's Embedding Theorem. The main techniques include mutual information, false nearest neighbors, forward and reverse Lyapunov exponents, and phase-space reconstruction (see Figure 2).

One of the difficulties encountered during this study was the size of the HHA time series data set. While a large number of data points were collected, only small subsets (less than 5,000 sequential points) exhibited nonuniform dripping behavior. In order to test the selected chaos techniques before assessing the HHA data set, we used a clean, long, noise free data set from an aluminum weld process.



Gc00 0701

Figure 2. Example of chaotic tools used for inferring dynamics within sampled signals.

After validating the general analysis procedure, we evaluated the HHA data set. The measured dynamics (drip intervals) of the HHA data were integrate-and-fire dynamics instead of direct state measurements as in our original test system. Basically, integrate and fire means that instead of measuring a state variable directly, such as pressure or flow, the HHA data set was a measure of the culmination of these state variables in the form of a drip. Taken's Embedding Theorem does not directly apply to an integrate-and-fire data set. We began a detailed study of what type and amount of integrate-and-fire dynamics are needed to reproduce a Taken's style embedded phase space under Sauer's new integrate-and-fire embedding theorem.³ In order to address this and further validate the desired test procedure, we returned to our welding test system, which also exhibited integrate-and-fire dynamics. Weld measurement data were in the form of droplet detachment events, just as the data in the HHA data set. For the traditional Lorenz and Rössler Systems, there is a basic requirement of at least 50,000 and 5,000 samples, respectively, for accurate estimates of the embedding dimension (see Figure 3). However, as with the HHA data set, our current welding data set did not contain enough useable integrate-and-fire dynamics to result in conclusive answers about the system.

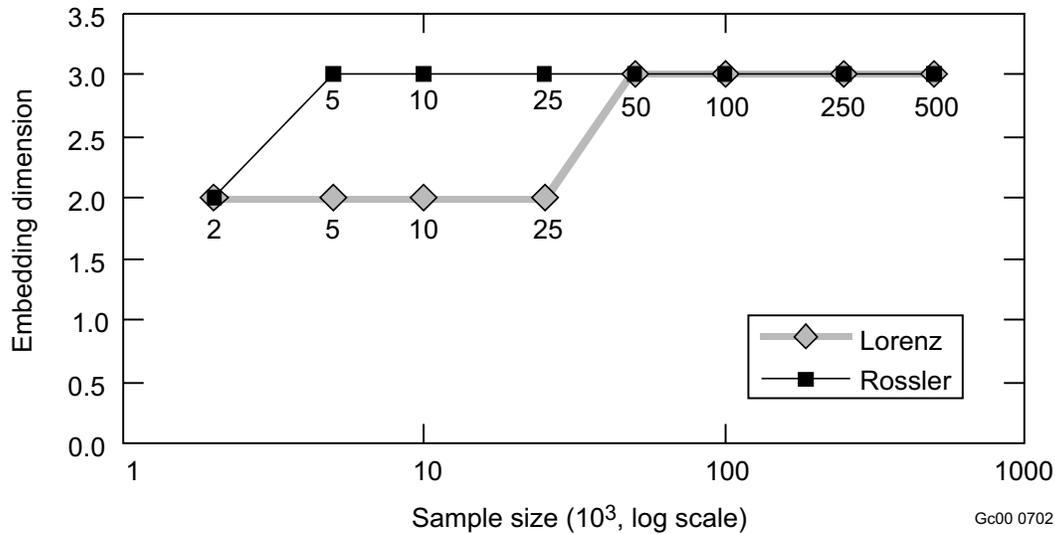


Figure 3. Plot showing the size of data sets required to estimate the correct embedding dimension for the Lorenz and Rossler chaotic systems in thousands of samples: 50,000 and 5,000 samples are required respectively.

We have been able to reconstruct the attractor dynamics based on the integrate-and-fire measurements for the Rossler and Lorenz systems. This is a test case to verify the process for the drip data reconstruction effort. To date, it appears we do not have enough data to proceed with attractor reconstruction with the drip data. Traditional chaotic analysis of environmental data is problematic because of the extreme length of data sets required and the need to measure state variables directly.

Subtask 3. A Numerical Technique to Screen Time Series Data for Nonlinear Behavior

The goal of this work is to develop and implement methods that could quickly screen time series data for signs of significant nonlinear behavior. With such methods, large data sets could quickly be screened for nonlinear behavior and these parts of the data sets more carefully analyzed, as in Subtask 2. Our approach was to compare empirical time series with surrogates generated under various hypotheses. The idea is to choose hypotheses that correspond to trivial or linear dynamics, so that the failure of the original data to agree with the surrogate is taken as an indication of nontrivial and, possibly, complex behavior. In order to define what agree with means, one needs to consider a statistic capable of discriminating between complex and trivial dynamics. A robust statistic employed to study time series for complexity is approximate entropy (ApEn), developed by Steve Pincus. ApEn can be viewed as the average of the log of the conditional probability that a particular pattern exhibited in a time series persists given that it occurred before. Therefore, ApEn is at a maximum when all patterns are available; ApEn is minimal when only one pattern is found. Therefore, ApEn is a measure of disorder in a series of symbols.

We tested the idea of ApEn as a discriminating statistic in a variety of contexts. We generated surrogate data according to the hypothesis that the dynamics are linear. Therefore, we generated surrogate data subject to the condition that they yield the same spectrum (and autocorrelation function) as the original data. Our tests included random systems, periodic systems, the logistic map, the Henon map, the Rossler system, the Lorenz system, and the Mackey-Glass system. The results show that the failure of the linear-dynamics hypothesis under ApEn is sufficient but not necessary to identify nonlinear dynamics. The linear dynamics surrogate data method requires that the original data be evenly spaced in time; this is

not the case for many data of interest. For this reason, among many others, it is important to investigate the performance of ApEn and other statistics, as we are now doing, with alternative hypotheses under which surrogate data may be generated.

Subtask 4. Evaluation of Theoretical Low-Dimensional Dynamics

The purpose of this subtask is to develop a theoretical model that will not harbor environmental noise nor be limited by short data sets. Preliminary analysis of the HHA droplet interval data suggests the possible existence of a low-dimensional attractor. It is likely, however, that the existing data set contains sufficient sources of ambiguity or noise that no conclusive outcomes will be achieved. Irrespective of what the analyses show, it is important to consider the possibility that vadose zone flow is a low-dimensional process. A theoretical model for the HHA experiment may show, in autonomous form (no external driving), low-dimensional dynamics, while in the presence of external perturbations may be an example of self-organized criticality. The latter is especially interesting in terms of the long-range goals of subsurface science at the INEEL, because self-organized criticality behavior is scalable. That means that a series of laboratory experiments done on different mesoscales may allow correct inferences to be drawn about macroscale behavior. To begin, consider a system of substantial fame in the nonlinear dynamics literature—the dripping faucet. It has been known for many years that a slowly dripping faucet can exhibit complicated dynamics, purportedly ranging from simple periodic behavior to perhaps even low-dimensional chaos.⁴ Of course, the claim for low-dimensionality in real (as opposed to simulated) data is obscured by ever-present instrumental uncertainties and environmental variability. The claim is also confounded by the fact that a flowing fluid is thought to be aptly modeled by the Navier-Stokes equations, a set of partial differential equations. Systems of partial differential equations typically produce infinite- (not low-) dimensional dynamics, though there are circumstances under which such systems can become episodically low-dimensional. How this reduction occurs in the dripping faucet is not yet clear.^{5,6} Nonetheless, we will assume that in a clean, well-controlled experiment the fluid dynamics of drop formation is low-dimensional, and that drop formation can somehow be adequately described by a small set of ordinary differential equations.

It is extremely unlikely that a single faucet dripping model will adequately capture the essence of the HHA data set. The HHA experiment is performed in complex soil, consisting of fractured and porous rock and loosely bound grains. The flow paths through this test bed vary in cross-section and roughness. The flow is undoubtedly multiphasic with complicated wetting characteristics, and possibly evaporation.⁷ Furthermore, the dripping into the cavity below the test bed occurs at multiple sites, not at a single orifice.

We will present a model developed to approximate the spatial variability of the HHA experimental conditions. The model is a modification of one that has been employed to study imbibition fronts of fluid climbing up vertical filter sheets.^{8,9} In this model, the medium is represented by a square lattice of pipes oriented at 45 degrees, as shown in the Figure 4. The nodes in the lattice are at the intersection of four pipes (except at the surfaces, where they are at the intersection of two pipes) and are assumed to contain no volume. The network scheme can be combined with the dripping faucet model to obtain a better approximation to the HHA dripping experiment than provided by the latter alone. In this figure, each of the output nodes is a faucet, and each drips according to the scenario for a single faucet. The driving parameter for each node is the total mass flow into that node from the two pipes connecting to it. Some nodes will have very low flow rates, while others will have larger rates. Drop detachment will be asynchronous over the entire set of output nodes. Depending on the network configuration and imposed pressure difference between the top of the test bed and the cavity, all output nodes may be dripping periodically, some periodically and some chaotically, or all chaotically. Such a system will have very rich dynamics indeed. The network model described here can be modified so that flow changes in one pipe affect flow in neighboring pipes. It would be very interesting to see if such a model has self-organized

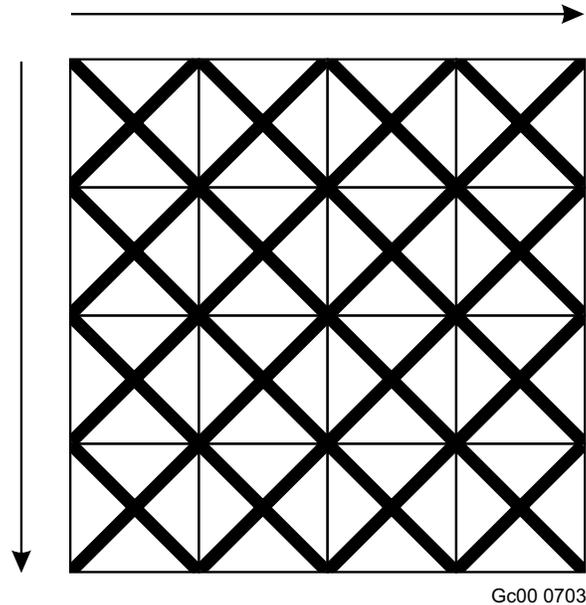


Figure 4. A square lattice of pipes oriented at 45 degrees.

criticality characteristics. If it does, and if such a network aptly models the HHA experiment, then the impetus for constructing several mesoscale experiments that investigate forecasting and control would be made much more compelling.

Subtask 5. A Theoretical Evaluation from First Principles for Complex Behavior

The purpose of this subtask is to determine whether the governing equations of vadose zone flow and transport, which are related in nonlinear fashion, will act to generate chaotic dynamics. This analysis is similar to the analysis performed by Lorenz on governing equations of convection cells in the atmosphere. We first performed a literature survey in scientific journals to identify previous work on employing methods of nonlinear dynamical systems theory to model flow in porous media. We found several articles where nonlinear dynamics had been applied to the results of experimental data, but none were found that attempted a first-principle analysis as we propose. This gave us encouragement to proceed to identify rational methods of reducing the governing nonlinear equations of flow in porous media. Key to performing a nonlinear analysis is to reduce large dimensional governing equations into a set of low-order ordinary differential equations. We investigated three techniques: the center manifold reduction, parabolized stability technique, and proper orthogonal decomposition. The center manifold method seems to be the most robust. We are continuing to pursue this subtask, having the ultimate goal of being able to generate noise-free data sets using surrogate values.

ACCOMPLISHMENTS

Our accomplishments during FY 2000 are as follows:

- We observed that several examples of vadose zones across the DOE complex show characteristics of complex, nonlinear systems.

- We presented our work at the National Geological Society of America Annual Meeting (see Appendix A).
- We used well data to verify applicability of the chaos analysis toolbox to the characterization of vadose zone. Because of the limited number of data available for HHA, a rigorous evaluation of this data set for chaotic properties is not possible with the analysis tools we are validating.
- The majority of time delay traces in the HHA data set exhibit evidence of periodic or discrete behavior, as indicated by a formal mathematical evaluation.
- Several governing equations for flow in porous media could be transformed for flow in fractured media such as that observed at HHA.

REFERENCES

1. *From Cleanup to Stewardship, A Companion Report to Accelerating Cleanup: Paths to Closure and Background Information to Support the Scoping Process Required for the 1998 PEIS Settlement Study*, DOE, 1998.
2. *Research Needs in Subsurface Science*, U.S. Department of Energy, Environment Management Science Program, Board on Radioactive Waste Management Water Science, and National Research Council Technology Board, ISBN 0-0309-06646-8, 2000.
3. Timothy Sauer, "Reconstruction of Integrate-and-Fire Dynamics," George Mason University, Department of Mathematical Sciences, <http://math.gmu.edu/~tsauer/pre/index.html>, 2000.
4. R. S. Shaw, "The Dripping Faucet as a Model Chaotic System," Santa Cruz: Ariel, 1984.
5. S. D. R. Wilson, *Journal of Fluid Mechanics*, Vol. 190, 2000, p. 561.
6. N. Fuchikami, S. Ishioka, and K. Kiyono, *Journal of the Physical Society of Japan*, Vol. 68, No. 4, April 1999, pp. 1185–1196.
7. D. Or and T. A. Ghezzehei, *Water Resources Research*, Vol. 36, 2000, p. 381.
8. E. Aker and K. J. Måløy, *Physical Review E*, Vol. 58, 1998, p. 2217.
9. C. H. Lam and V. K. Horvath, *Physical Review Letters*, Vol. 85, 2000, p. 1238.

Ecological Engineering of Rhizosphere Systems

Engineering Root-Soil Systems for Use in Remediation

**Melinda A. Hamilton, Richard Hess, Carl Palmer, Neal Yancey (INEEL);
Paul Bertsch (Savannah River Ecology Laboratory)**

SUMMARY

Phytoremediation, or using plants to clean up metals in contaminated soils, is becoming a more common bioremediation method at a variety of DOE sites. Planting a ground cover over closed low-level waste sites for long-term stewardship is a very attractive option because of its low maintenance and the added benefit of erosion control. However, the effectiveness of using plants in such a way is hampered by a lack of knowledge of the fundamental processes occurring in the plant root-contaminant interactions. By conducting basic research into plant root systems, this research task will eventually lead to cost-effective technology for remediation of dispersed radionuclide/heavy metal contamination in soil.

The purpose of this task is to acquire the fundamental scientific understanding needed to exploit rhizosphere processes for developing cost-effective remediation technologies that can be used to remediate dispersed radionuclide and or heavy metal contamination in soil. Understanding rhizosphere processes will allow us to predict and improve the long-term performance of ground cover planted over closed low-level waste sites. This ground cover provides the primary barrier against erosion by wind, water, etc., which could compromise the integrity of the site. It is also the final barrier against the upward migration of contaminants left in place, which, if unimpeded, could begin to affect the environment and potentially human health. The knowledge gained from this task will help us model the fate and transport of such contaminants through the soil, help us better understand the biotic component of the ecosystem, and provide low capital and operating cost ecosystem-based technologies to a wide variety of users, including DOE, the Department of Defense, mining industry, oil and gas industry, and U.S. Department of Agriculture. This task will advance ecological engineering technologies that are unique, competitive, and address pressing environmental problems and demands.

This task includes ecosystem dynamics (an ecological approach to understanding biological interactions), rhizosphere biology (interdependent plant and microbe physiology), and geochemistry (abiotic affects on plant nutrition and soil microbiology). The initial research subtasks for this task are (a) selecting a simple, two organism rhizosphere system for investigation, (b) characterizing analogous natural rhizosphere systems, (c) assembling simplified artificial systems in the laboratory and measuring system performance, and (d) developing a conceptual model of ecosystem performance.

TASK DESCRIPTION

The objective of this task is to develop innovative “ecological engineering” approaches for designing rhizosphere systems based on “ecological packets” (multiorganism communities that collectively achieve difficult survival and or remediation functions). To obtain our objective, we are focusing our research on determining the associations (symbiotic and antagonistic) between biological components (plant and microbe) and the affecting abiotic factors of the environment they come from and will be expected to perform in. Understanding these multiorganism rhizosphere processes is key to engineering the combination of biotic and abiotic factors that will guarantee the ecological fitness of the biotic components and system performance in the ambient environment. The environmental remediation applications for soils contaminated with metals and mixed-waste represent a logical area to initiate ecological engineering of rhizosphere systems. Understanding and successfully modeling plant/microbe

survival, competitive dominance, and symbiotic and or antagonistic interactions are key factors in successfully developing in situ biological remediation technologies. The initial research subtasks for this task are (a) selecting two simple organism rhizosphere systems for investigation, (b) characterizing analogous natural rhizosphere systems, (c) assembling simplified artificial systems in the laboratory and measuring system performance, and (d) developing a conceptual model of ecosystem performance.

There are three research elements we consider imperative to developing an understanding of rhizosphere ecology sufficient to allow engineering of rhizosphere systems: ecosystem dynamics (an ecological approach to understanding biological interactions), rhizosphere biology (interdependent plant and microbe physiology), and geochemistry (abiotic affects on plant nutrition and soil microbiology). An integrated approach to studying these three research elements requires not only a multidisciplinary tactic, but also a multi-institutional program.

The variety of users that could benefit from low capital and operating cost, ecosystem-based technologies include DOE, Department of Defense, mining industry, oil and gas industry, and U.S. Department of Agriculture. This effort will advance ecological engineering technologies that are unique, competitive, and address pressing environmental problems or demands.

Selected INEEL Rhizosphere Ecosystem

We selected a model rhizosphere system with parameters that could be assembled in the laboratory and investigated with sufficient control to reduce factors that may confound experimental results. The model system is also practical and relevant to cesium (Cs) contamination in INEEL soils. A crested wheatgrass (*Agropyron cristatum*) ecosystem growing in and around Cs contaminated soil was selected. Crested wheatgrass is a perennial bunch grass native to the steppes of Asia and very tolerant of high temperatures and low moisture content, typical of the arid environment of the INEEL and Intermountain West (see Figure 1). This model rhizosphere system is of interest to DOE, and even more so, the INEEL. INEEL field sites at Waste Area Group (WAG) 5 (SL-1) and the Central Facilities Area (CFA) drainfield (CFA-08; WAG 4) were chosen for evaluation of the agronomic and ecological parameters of the crested wheatgrass ecosystem.



Figure 1. A planted crested wheatgrass stand on a disturbed site outside the radiologically contaminated area at SL-1 (INEEL WAG 5).

Field Characterization of the Selected INEEL Rhizosphere Ecosystem

Results from the detailed characterization of the natural rhizosphere system will support the selection of ecological and physicochemical components that must be incorporated into a growth chamber and or greenhouse based physical model rhizosphere system. First, modeling and simulating ecological population dynamics and physicochemical response curves of key plant and microbe nutrients and growth factors that affect symbiotic and or antagonistic associations will be used to mimic the natural system in the laboratory. From that laboratory baseline, we will then use the computer model developed in the following task as a basis for generating hypotheses to be investigated in the laboratory rhizosphere system. These laboratory manipulation studies will define the desired biological and abiotic factors and their associated temporal profiles to facilitate survival, competitive dominance, and symbiotic functions that extract Cs from soil under a wide range of potential “real-world” conditions.

Mineralogy of the Site

There have been several mineralogical analyses of surficial materials, sedimentary interbeds, and basalt at the INEEL site (see Table 1). Bartholomay et al. summarized these analyses and used the results with additional analyses to determine the correlation of different geological units with potential source areas.¹ The channel and overbank deposits of Birch Creek are coarser than those from Little Lost River.² Birch Creek sediments generally had a greater amount of quartz and calcite but less feldspar and dolomite than Little Lost River sediments. In both watersheds, illite is the dominant clay. Kaolinite and a mixed layer illite/smectite (I/S) were more common in the Little Lost River sediments. The sediments associated with the Big Lost River reflect the volcanic source rocks and generally contain more feldspars and pyroxenes.³ The mineralogy of the sedimentary interbeds at Test Area North correlate with the Birch Creek drainage while those at the Radioactive Waste Management Complex (RWMC), Test Reactor Area, and Idaho Chemical Processing Plant (now Idaho Nuclear Technology and Engineering Center) correlate with the Big Lost River drainage (see reference 3). Bartholomay suggests that the sedimentary interbeds at the INEEL site were deposited in a depositional basin similar to the present day basin.

Table 1. Summary of types of mineralogical analyses reported by Bartholomay et al. (see Reference 1)

Type of Analysis	Analyses No.	Comments
Bulk Mineralogical	117	
Clay Mineralogy	204	
Silt Mineralogy	56	
Cation Exchange	328	
Other	108	Bulk soil chemistry, specific gravity of soil particles, grain size

The sediments near the SL-1 site are mapped as loess.⁴ These windblown materials were likely derived from the sediments of the Big Lost River, Little Lost River, and Birch Creek. The analyses from a pit and cores near RWMC are likely to be the most useful for determining the potential mineralogy at the rhizosphere study site.⁵

The stratigraphy within the pit indicates the presence of two paleosols, one at 2.13 to 2.90 m below ground surface and a second at 4.33 to 5.55 m below ground surface (see Reference 5). These paleosols are distinguished by their reddish-brown color and by the low carbonate contents. The absence of carbonate suggests formation occurred during periods of greater infiltration rates. The bulk soil

mineralogy (see Table 2) is comprised primarily of quartz, with minor amounts of plagioclase, calcite, K-feldspar, and pyroxene (likely diopside). Between 25 and 70% of the sediment is comprised of clay-sized material. Powder x-ray diffraction of the clay fraction indicates that illite and mixed I/S clays are common (see Table 3). Smectite and kaolinite are also present in the soil. The cation exchange capacity (CEC) of the clay fraction of the sediments range from 11 to 27 meq (100 g)⁻¹ while the carbonate content ranges from 0 to 36%. Some of the mineralogical analyses also report detrital mica (see Reference 1).

Table 2. Ranges of the mineralogical composition of the clay fraction of the loess from Pit 15 at RWMC (see Reference 5).

Phase	% of Clay Fraction
chlorite	0
illite	30 to 36
mixed I/S	30 to 48
smectite	13 to 26
kaolinite	6 to 12

Table 3. Ranges of the bulk mineralogical compositions of loess from Pit 15 at the RWMC (see Reference 5).

Phase	%
quartz	15 to 29
K-feldspar	0 to 6
plagioclase	6 to 12
calcite	0 to 13
pyroxene	4 to 9
clays	25 to 70

Mineralogical analyses of core samples of the sedimentary interbeds show compositions similar to the sediments from the pit. Some additional observations include traces of olivine, hematite, siderite, the presence of amorphous and cryptocrystalline iron hydroxides, and weathered olivine with a residual iron hydroxide.

Based on these previous studies, we expect that the surficial sediments at the rhizosphere study site will be comprised of quartz, feldspars, pyroxenes, and clays; the clays will be predominantly illite and mixed I/S with some smectite and kaolinite; some micas may also be present in the soil; and paleosols containing increased amounts of iron hydroxides, but relatively low amounts of calcite, may exist within a few meters of the surface.

Soil and Plant Sample Collection and Analysis Methods

Sampling during FY 2000 was conducted on two plots in the uncontaminated zone surrounding the SL-1 burial ground—one disturbed and one undisturbed. The disturbed plot contains considerable gravel, and is bound by gravel roads on three sides and an exclusion fence on the fourth. The area has been scraped and planted with crested wheatgrass that now constitutes the dominant plant species within the plot. The undisturbed site is about 200 m north of the disturbed site, and is characterized by a native

sagebrush and or steppe plant community common to the INEEL. Both plots were located using geodetic survey point (GSP), and mapped using geographical information system (GIS). The purpose of including both a disturbed and an undisturbed site in the study is to determine the effects of disturbance on the various processes that influence Cs uptake. A site within the SL-1 CERCLA area known to be contaminated will be added during FY 2001.

Eleven sampling points were identified and marked with flags within the disturbed site. Additionally, three 25 ft vegetation transects were established within the plot. These transects were used to determine plant cover on a monthly basis. The sampling points and transects were selected to provide a reasonable representation of the plot, and were spaced so as to lend to spatial interpolation or kriging. One of the 11 sampling points was subsequently eliminated because sampling at that location was found to influence the transect data. The boundaries of the undisturbed site were selected to approximate the size of the disturbed site. Because the undisturbed site appeared to be much more homogeneous than the disturbed site, nine sampling points were selected systematically within the plot. Three transects were also established within the undisturbed site.

Samples were collected monthly at both uncontaminated sites (disturbed and undisturbed) starting in July 2000. Samples collected included bulk soil for nutrient analysis, bulk soil for microbial analysis, wheatgrass rhizosphere soil for nutrient analysis, wheatgrass rhizosphere soil for microbial analysis, and above-ground wheatgrass tissue for nutrient analysis. During the initial sampling, all 20 points (11 disturbed and 9 undisturbed) were sampled. In subsequent sampling, samples were collected at only six sample points in each of the two sites because of the time required to process the microbial samples. Plant community structure was determined monthly for all six transects using the line-intercept method.

Soil and vegetation analyses were conducted under contract by Western Laboratories of Parma, ID using established analytical methods.⁶ Soil nutrient analyses included nitrate (NO_3^-) ammonium (NH_4^+), P, K, Ca, Mg, Na, Zn, Fe, Mn, Cu, sulfate (SO_4^{2-}), B, as well as measures of pH, texture, salts, cation exchange, percent lime, percent organic matter, percent base saturation, percent Ca of CEC, percent Mg of CEC, percent K of CEC, and percent Na of CEC. Analysis of plant tissues included macro- and micronutrients.

Soil Microbial Analysis Methods

For bulk soil samples, approximately 1 g of soil (weighed) was suspended in 100 mL of sterile distilled water and shaken for approximately 20 minutes. From this suspension, serial 10-fold dilutions were made by transferring 0.5 mL into 4.5 mL sterile distilled water in a fresh tube. Triplicate 0.1 mL aliquots from appropriate dilutions were then inoculated onto plates using a spreader, and the plates incubated at room temperature for 2 to 3 days. For the rhizosphere soil samples, approximately 8 to 12 g of roots with their associated monolayer of soil were cut from the root mass, weighed, and put into sterile flasks along with 100 mL of sterile distilled water. The flasks were shaken for approximately 20 minutes to wash off and suspend the microorganisms; the 100-mL sample was then treated the same as for the bulk soil. After all inoculations onto the plates, the roots were thoroughly rinsed over a screen, blotted, allowed to air dry, and weighed. The weight of soil dislodged from the roots (and thus sampled) was calculated by difference. Selected dilutions from each sample were inoculated onto plates containing four different types of media: 1/10 strength tryptic soy agar, to enumerate total heterotrophs; 1/10 tryptic soy agar containing neutral red, to look for acid producers; minimal medium containing 1 g/L phenol as a sole carbon and energy source, to enumerate phenol degraders; and minimal medium containing a mixture of three organic acids (citric, succinic, and lactic) as sole sources of carbon and energy, to enumerate organic acid metabolizers.

Modeling Cesium Bioavailability as Affected by the Rhizosphere Ecosystem

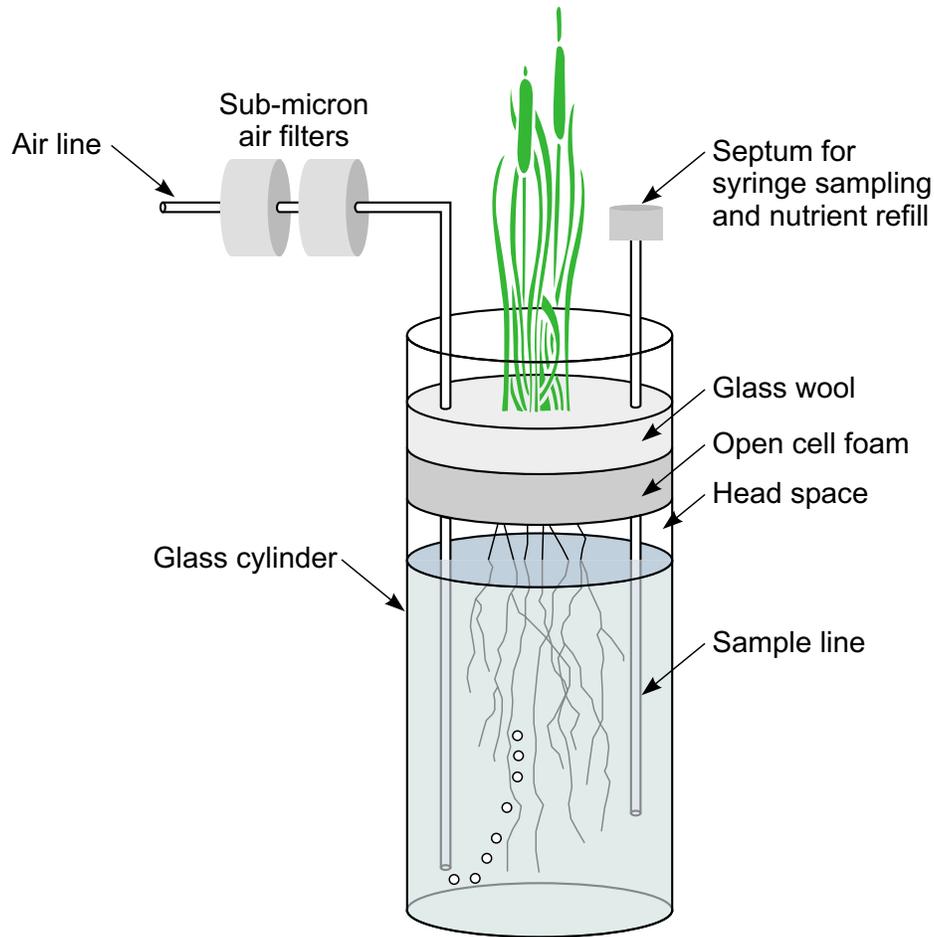
The goal of this effort is to model the geochemical, biological, and physical factors affecting Cs solubilization in the rhizosphere. The specific objectives to accomplish the goal are to (a) develop a comprehensive conceptual model that integrates the various effects on Cs solubilization, (b) develop a quantitative mathematical model relating root exudates and Cs solubilization, and (c) incorporate the exudate model into the comprehensive model. The conceptual and quantitative models will be implemented iteratively for validation and refinement. The fundamental approach will be based on mass balance and transport equations (advection-dispersion-reaction).

To achieve these objectives, the factors and relationships affecting Cs solubilization must first be identified. Subsequently, it is necessary to select those assumed to warrant inclusion in the comprehensive conceptual model. A model rhizosphere system must also be chosen such that the parameters of the model plant/soil system to be studied can be investigated with sufficient control. A preliminary conceptual model will establish basic associations using software that allows these relationships to be set up in sectors, with each sector representing a submodel. Available data will be used to determine functional relationships within and between submodels. Parametric values will be evaluated only for functional relationships that are well understood and properly presented in the literature or experimental data. The conceptual model code will be validated and the performance will be evaluated and refined as needed. To develop the exudate model, field and experimental data will be used to characterize exudate production and fate in the rhizosphere system. The rate of binding and release of Cs⁺ from phyllosilicates, commonly found at INEEL and DOE sites and known to bind Cs, will be quantified. A mathematical model relating the aqueous concentration and release rate of root exudates to Cs solubilization will be developed based on field and experimental data. Using additional experimental data, the equation(s) will be solved and the results used to evaluate and update the specific model. Finally the mathematical exudate model will be incorporated into the comprehensive conceptual model, which will then be evaluated and refined as needed.

Laboratory Assembly of a Hydroponic System for Rhizosphere Exudate Studies

Creating and maintaining sterile conditions in the plant root zone is a challenging task. The root-zone environment is ideal for the rapid growth of a wide range of microorganisms.⁷ Creating sterile conditions requires that all parts of the project apparatus and the germinating seedlings be sterile. The project apparatus will be constructed using inert, autoclavable materials, which will be autoclaved prior to each study. Obtaining sterile seedlings is more challenging. Seeds will be surface sterilized and grown on nonselective agar to confirm that seed associated microorganisms have been effectively removed. A brief soak in 10% Clorox (5.25% sodium hypochlorite) is adequate to sterilize some seeds, but more aggressive techniques are often required. These techniques include a preliminary soak in 50% ethanol to dewax the seed coat, soaking in 0.2% HgCl₂ with Tween 80 wetting agent, and suspending seeds over a solution of sodium hypochlorite and then injecting acid in a sealed container to produce chlorine gas, which penetrates the seed coat more effectively than liquid solutions.

After exposure to the sterilizing environment, seeds will be thoroughly rinsed in sterile deionized water and germinated on nonselective agar to confirm sterility. The safest, most effective, seed treatment procedures will be identified and used in subsequent studies. After germination, seedlings will be transferred in a sterile hood to sterile plant growth containers that we have custom designed for these studies. A diagram of the proposed culture vessel is shown in Figure 2.



Gc00 0694

Figure 2. Sterile hydroponic/solid media culture system from which plant secreted exudates can be recovered.

Our proposed sterile plant culture container is modified from similar designs used by other workers (see Figure 2).^{8,9,10} The incoming air will be filtered through two 0.2-micron filters connected to a stainless-steel syringe. Only a small air flow (about 50 mL/min) is needed to maintain oxygen saturation in the root zone. This airflow will positively pressurize the root zone and minimize the downward movement of air and microorganisms to the surface of the container. The hydroponic solution will be separated from a foam support plug by an air gap (headspace). This gap, along with a slight temperature difference due to the growth chamber lights heating the plug, will keep the foam plug and glass wool dry, which further minimizes the potential for contamination. Since root growth is inhibited by light, the glass container will be covered with aluminum foil to keep the roots in the dark.

A dilute nutrient refill solution will be added daily to replenish the solution removed in transpiration. We have done extensive work to develop the composition of this solution so that it replaces both the nutrients and the water without the need to drain and replace the entire contents of the container.^{11,12,13}

The same apparatus will be used for studies in solid porous media. These studies will be conducted by filling the root-zone volume with either small diameter glass beads or silica sand. The root-zone water status will be maintained by daily addition of nutrient solution to replace transpiration. Water loss in

transpiration will be determined by periodic weighing of the vessels. The use of a relatively inert substrate, such as glass beads, is important to the recovery of exudates, which quickly bind to organic matter and clays in soils. Exudates will be recovered by drawing a solution sample from the porous media.

Integrating Rhizosphere R&D With Operations to Solve INEEL Remediation Challenges

Where We See the Work Going Beyond ESRC

No new funding is being sought through laboratory directed research and development for FY 2001. Plans are to continue this task in FY 2001, continue to pursue work with the Environmental Restoration group at the INEEL (WAG managers) to conduct phytoremediation feasibility studies on site, and to prepare and submit funding proposals for FY 2002, which will go to: Natural and Accelerated Bioremediation, Environmental Management Science Program, and Subsurface Contaminants Focus Area.

The goal of this task is to develop a sufficient understanding of rhizosphere processes to allow the prediction, modeling, and ultimately, the control of contaminants in the rhizosphere. The rhizosphere can be viewed as the window to the vadose zone. The knowledge gained will lead to the development of cost-effective technologies for remediation of dispersed radionuclide and or heavy metal and mixed waste contaminated soil both in vegetated surface soil and subsurface soil. Current focus on Cs bioavailability directly supports Site Technology Coordinating Group, Need Statement ID-6.2.08, which expresses a need for understanding the mechanisms that control Cs binding and the need for removal technologies. Cs contamination is the number one contaminant (by number of sites) both at the INEEL and across the DOE complex. At the INEEL alone, there are more than 25 soil plumes known to have Cs contamination.

In recent discussions with the INEEL manager of Waste Area Group (WAG) 4, it was discovered that a drainage area contaminated with Cs-137 has a Record of Decision (ROD) that is considered by WAG management to be inadequate. They have requested that our team perform exploratory research this fiscal year to determine the potential of using phytoremediation as an alternative, and the extent to which native vegetation may be removing and or sequestering the Cs. It is expected that we will be funded for this work July through November 2000, at which time the review of the ROD will determine the follow-on funding for phytoremediation treatability studies.

Plans for the Remaining ESRC Funding

The scope of work for FY 2001 will entail:

1. Completing field characterization studies that spatially and temporally describe the biological components of the selected plant/soil system, including plant community dynamics, microbial community characterization, characterization of rhizosphere biota, and interactions.
2. Completing development of a conceptual model of the biological parameters that influence Cs bioavailability.
3. Completing the database and data analysis from site characterization and existing information.
4. Performing hypothesis driven experimental research to elucidate the influence of biological parameters (identified through site characterization, existing information, and conceptual

modeling efforts) on Cs fate and transport (focusing initially on root exudate interactions with Cs).

5. Constructing a simplified, artificial, physical rhizosphere system.

ACCOMPLISHMENTS

Characterization of In situ Rhizosphere Ecosystems

As discussed in the Task Description section, two study plots were established near SL-1, and their boundaries, sampling locations, and transects were located and mapped (see Figures 3, 4, and 5).

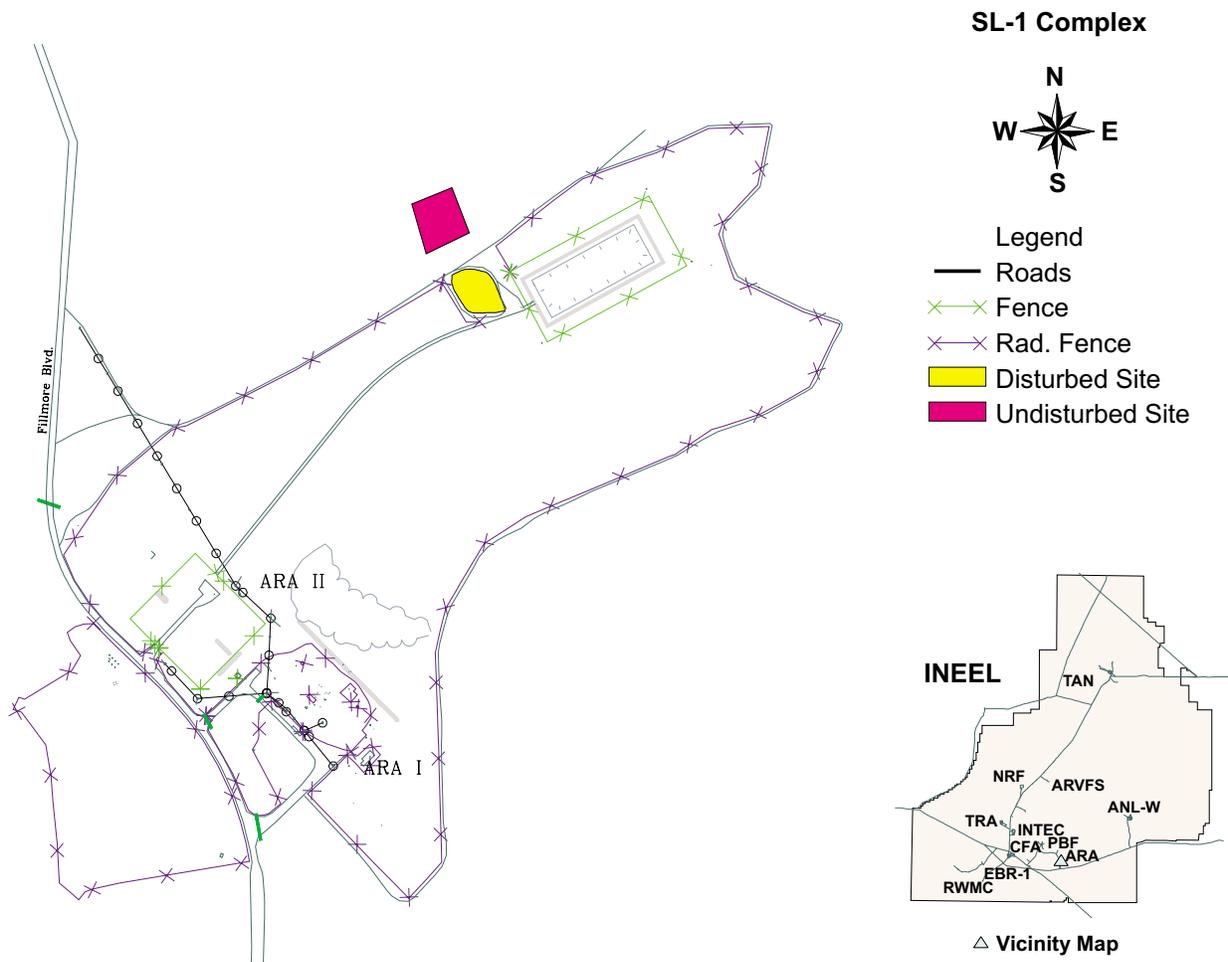


Figure 3. Study plot locations near SL-1

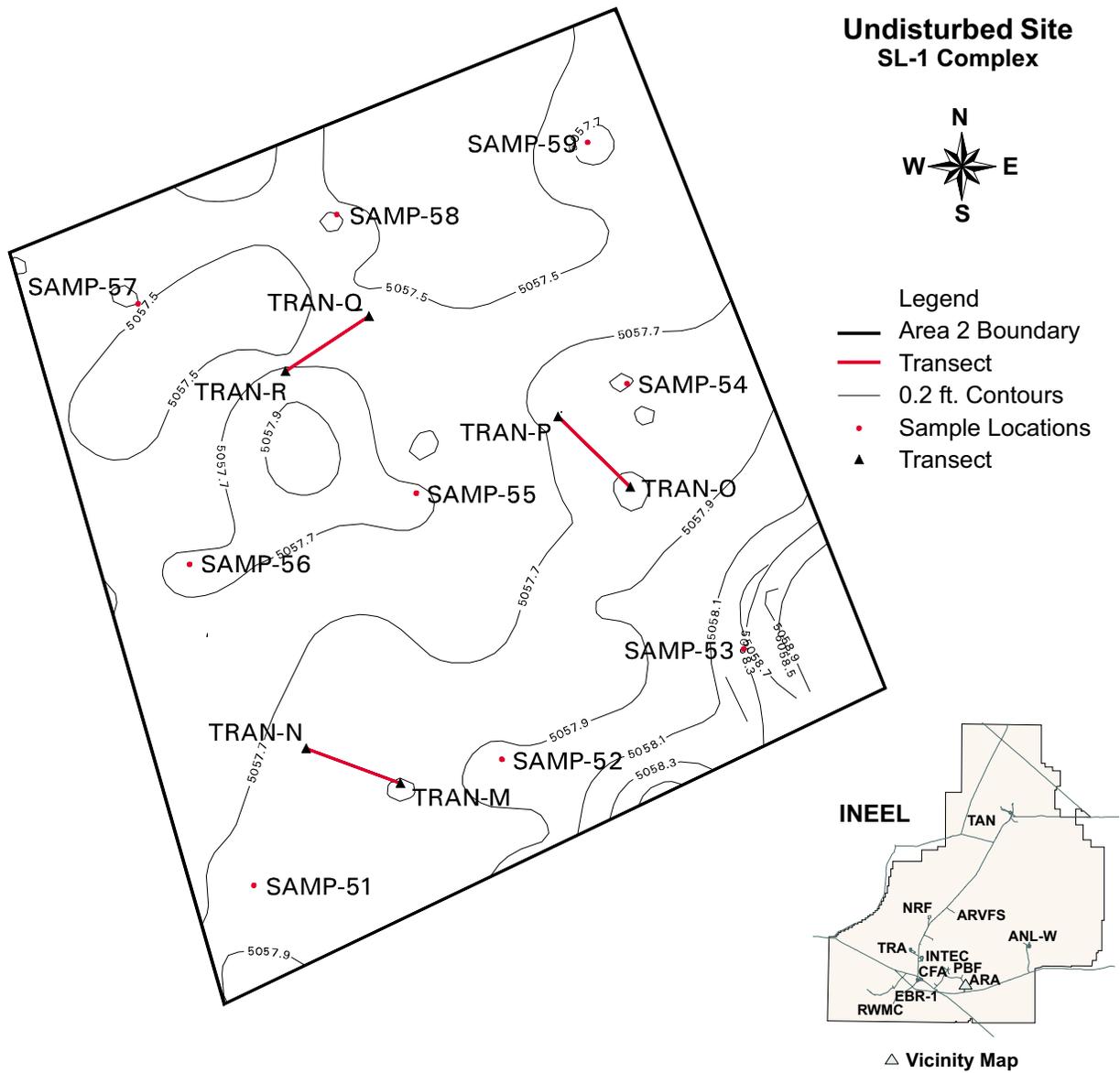
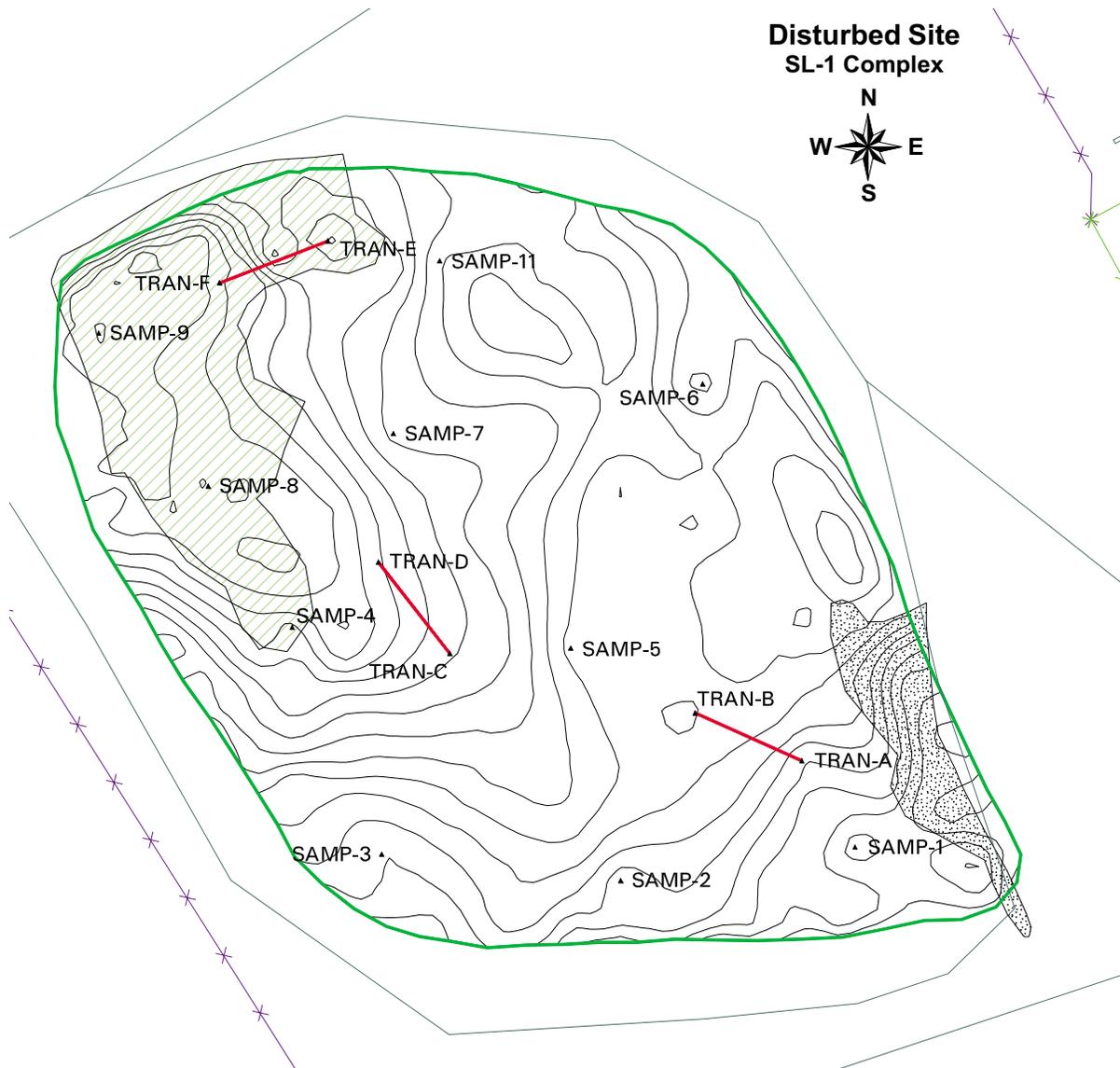


Figure 4. Undisturbed study plot showing sampling locations and vegetation transect.



- Legend
- Roads
 - ×—× Fence
 - ×—× Rad. Fence
 - Transect
 - 0.2 ft. Contours
 - Area 1 Boundary
 - ▨ Rabbit Brush
 - ▨ Gravel Pile
 - Sample Locations
 - △ Transect

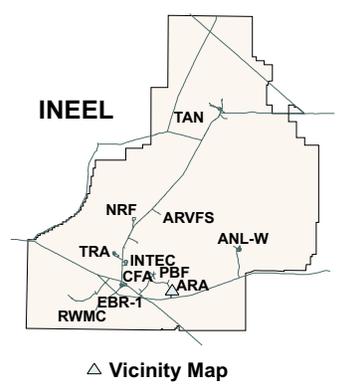


Figure 5. Disturbed study plot showing sampling locations and vegetation transect.

These plots are located in the vicinity of SL-1. An accident in January 1960 resulted in an approximately 100-acre area being contaminated with radiocesium. Previous radiological surveys of area soils have identified the highly contaminated area which is controlled (fenced with locked gate and the fenced area designated as a radiological controlled area) to limit personnel access.

Field characterization of the two plots outside this highly contaminated area was started during the summer of 2000. One plot was disturbed during the movement of materials from the SL-1 accident, as evidenced by the planted crested wheatgrass, a perennial bunchgrass native to the steppes of Asia. The second plot is undisturbed as evidenced by the prevalence of native sagebrush (*Artemisia* spp.) and fescue (*Festuca* spp.).

The third plot will be located within the highly contaminated area and will be characterized starting in the summer of 2001.

Soil Sampling Accomplishments

During July, August, and September 2000, 88 soil samples were collected and have been analyzed by Western Laboratories. The lab is presently analyzing another 12 samples collected in October.

As would be expected, the analyses show a much greater variability in most parameters among the samples from the disturbed site compared to the undisturbed site. An example of this is shown in the variability of K levels in the disturbed plot (see Figure 6) and the undisturbed plot (see Figure 7) where the variation in the disturbed plot was twice that in the undisturbed plot.

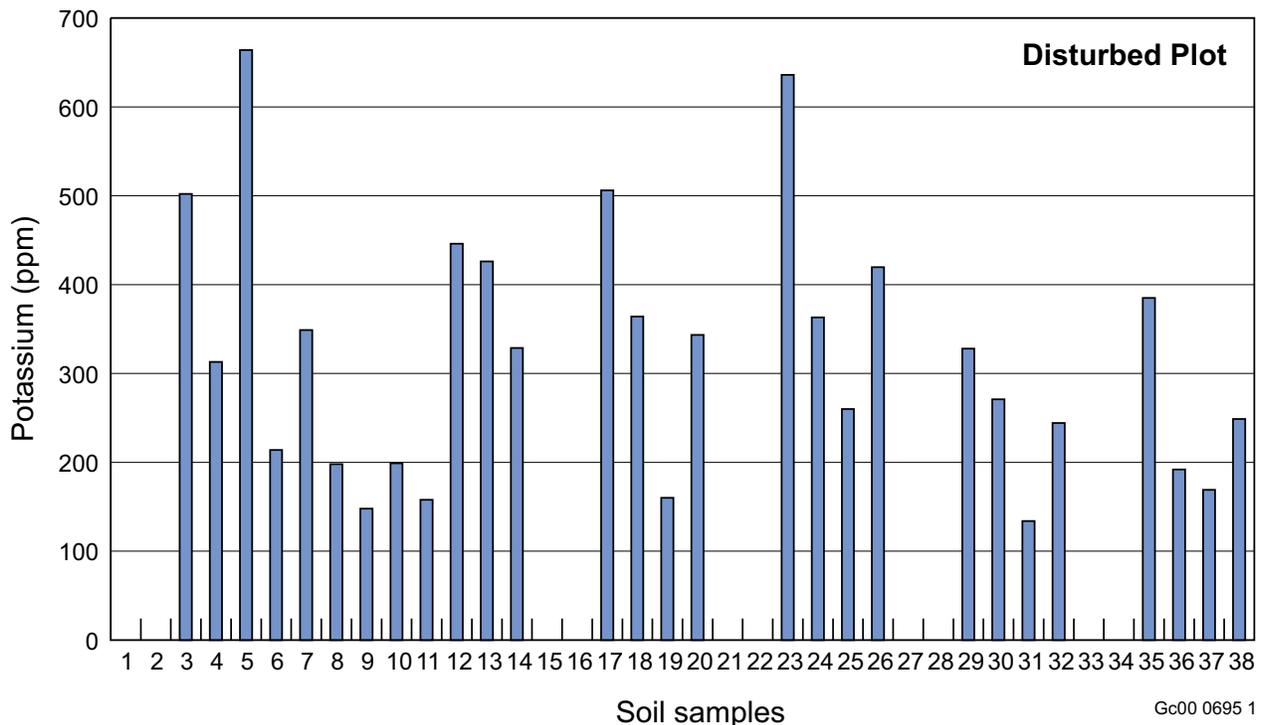


Figure 6. Variability of K among disturbed plot soil samples.

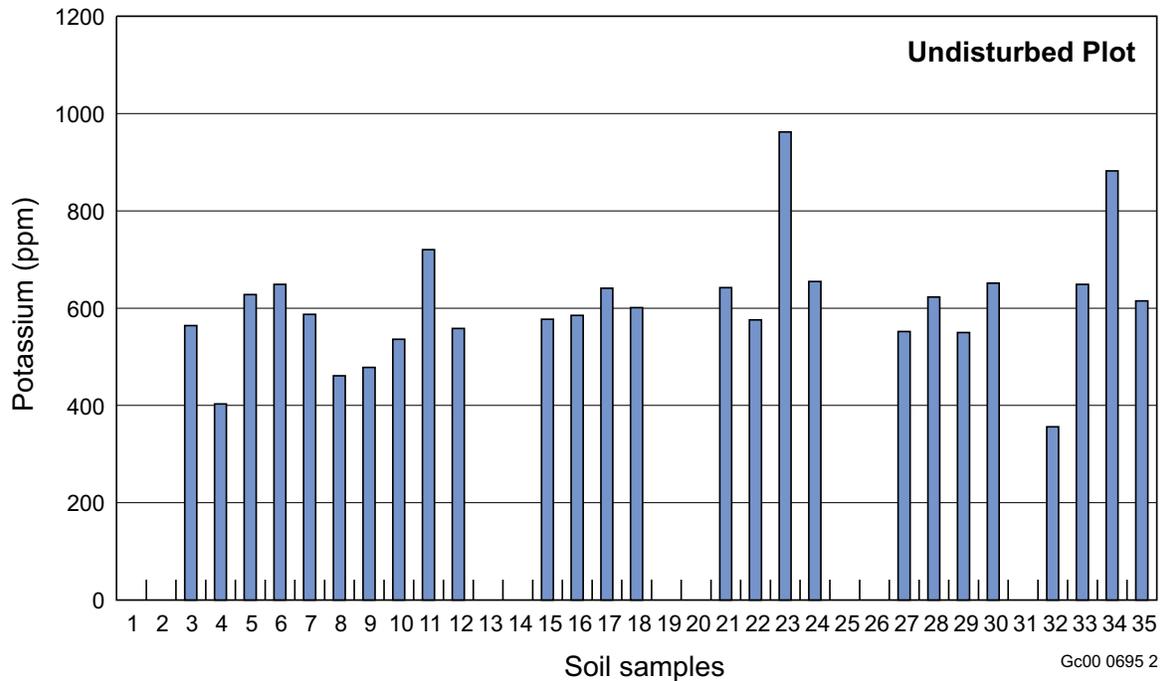


Figure 7. Variability of K among undisturbed plot soil samples.

The disturbed plot bulk soil K level averaged 321.1 ppm with a standard deviation of 154.3 ppm (coefficient of variation = 0.48). The undisturbed plot bulk soil K level averaged 601 ppm with a standard deviation of 137.6 ppm (coefficient of variation = 0.23).

The undisturbed plot rhizosphere soil K level averaged 912 ppm with a standard deviation of 151.7 ppm (coefficient of variation = 0.17). The variability in the rhizosphere soil K in the undisturbed plot is similar to that of the bulk soil K in the undisturbed plot, and the K is at a higher concentration in the rhizosphere soil mostly due to the plant's transport and uptake mechanisms.

Further soil data analyses and mapping is continuing, but the lessons learned from the FY 2000 field season on soil sampling are as follows:

- To better understand the spatial variation we must take frequent soil samples from all sample locations and have them analyzed, rather than restricting the sampling to the same number of samples that can be accommodated for microbial analyses.
- To better understand the temporal changes we must begin sampling as early in the season as possible and continue as late into the fall as possible.

Vegetation Sampling Accomplishments

Three vegetation transects were established in each of the two plots. Initially, the ends of the transects were marked with flexible plastic end posts, and the transect line was identified by a string tied taut between the two end posts. Movement of the end posts created movement in the transect line which affected the percent cover readings. Transect data collected in the summer showed that we were introducing too much variability due to the flexibility of the posts and string. Those data collected have been discarded as invalid. In September we installed rigid posts which remedied this problem.

The values presented in Table 4 reflect the averages from two transects in each area (disturbed and undisturbed). Two transect lines were resampled on 9/21/00 to check for variability between readings. Percent cover values from the 9/21 readings were within three percentage points of the readings on 9/13.

Table 4. Summary of vegetation transect data for September 2000.

Bare Ground or Species Present	Disturbed Plot (Percent Cover)	Undisturbed Plot (Percent Cover)
Bare ground	52.3	38.3
Rabbitbrush	16.3	8.7
Crested Wheatgrass	30.8	33.4
Fescue sp.	0.0	0.7
Sagebrush	0.6	19.0

These data show the high amount of sagebrush and fescue cover in the undisturbed plot (31.9% of cover) compared to the disturbed plot (0.001% of cover), the large amount of bare ground in the disturbed plot, and the preponderance of crested wheatgrass and Rabbitbrush cover in the disturbed plot (98.7% of cover) compared to 68.2% for the undisturbed plot.

Lessons learned from the FY 2000 field season on vegetation transect sampling are as follows:

- The transect line must be inflexible
- Methods must be established to measure the early season small ephemeral plants that will grow next spring for a short time period
- Other methods must be examined to better measure the plant community's composition, size, canopy, and root volume.

Microbial Analyses Accomplishments

Preliminary data from the microbial analyses of the bulk soil and rhizosphere soil indicate the following trends:

- For the bulk soil samples:
 - The heterotroph numbers are generally between 10^5 and 10^6 per gram.
 - Acid degraders and phenol degraders are uniformly very low, either below detection limits or between 10^3 and 10^4 per gram.
- For the rhizosphere soil samples (these numbers have not yet been corrected for the amount of soil sampled and will probably fall):
 - Heterotrophs are generally between 10^7 and 10^8 per gram, i.e., roughly 10 to 100× as many as in the bulk soil.
 - Phenol degraders are below detection limits in most samples.

- Numbers for the acid degraders varied more than for the heterotrophs. A majority of samples fell in the range of high 10^6 to low 10^7 , but a few were in the high 10^5 to low 10^6 . Generally acid degraders were in the range of 10 to 30% of the heterotroph counts, whereas in the bulk soil they were generally closer to 1% of the heterotrophs.

Several of the analyses cannot yet be interpreted because the numbers for the plates at the various dilutions do not follow the 10-fold dilutions used to generate the inocula.

Modeling Rhizosphere Affected Cs Bioavailability

After first identifying the key variables affecting Cs solubilization in the rhizosphere, we categorized the factors as geochemistry, physical, root system density, microorganisms, nutrients, and root exudates. We then selected the relationships within and between these categories assumed to warrant inclusion in the comprehensive conceptual model. This selection was based on hypotheses developed from the initial literature review.

The modeling effort is being implemented using Systems Thinking, which integrates the relationships between the many factors affecting Cs solubilization. To date, we have established the basic associations using software (Stella/iThink) based on this approach. The software (developed by High Performance Systems, Inc., Hanover, New Hampshire) allows for these relationships to be set up in sectors, with each sector representing a submodel. The submodels are defined as the six categories described in the previous paragraph, i.e., geochemistry, physical factors, root system density, microorganisms, nutrients, and root exudates. A seventh submodel is defined as Cs fate. The basic relationships within each submodel, as well as the interactions between submodels have been established (Figure 8). This approach allows for expertise in defining each sector, while simultaneously promoting the ecological packet. The model is ready for entry of the field characterization and experimental data.

While relationships affecting Cs solubilization are modeled within and between the six submodels, the solubilization itself is modeled in the “Cs fate” sector. The flow from the bound phase to the soluble phase reflects the principle that mass balance controls the fate of Cs, such that in a given volume of interest (e.g., $\mu\text{mol Cs/L}$ pore fluid):

$$Cs_{total} = Cs_a + Cs_w + Cs_i + Cs_p \quad (1)$$

Where:

Cs_{total} = total mass of Cs per volume of pore fluid

Cs_a = mass of aqueous Cs per volume of pore fluid

Cs_w = mass of weakly bound Cs per volume of pore fluid

Cs_i = mass of tightly bound, interlayer Cs per volume of pore fluid

Cs_p = mass of phytoextracted Cs per volume of pore fluid.

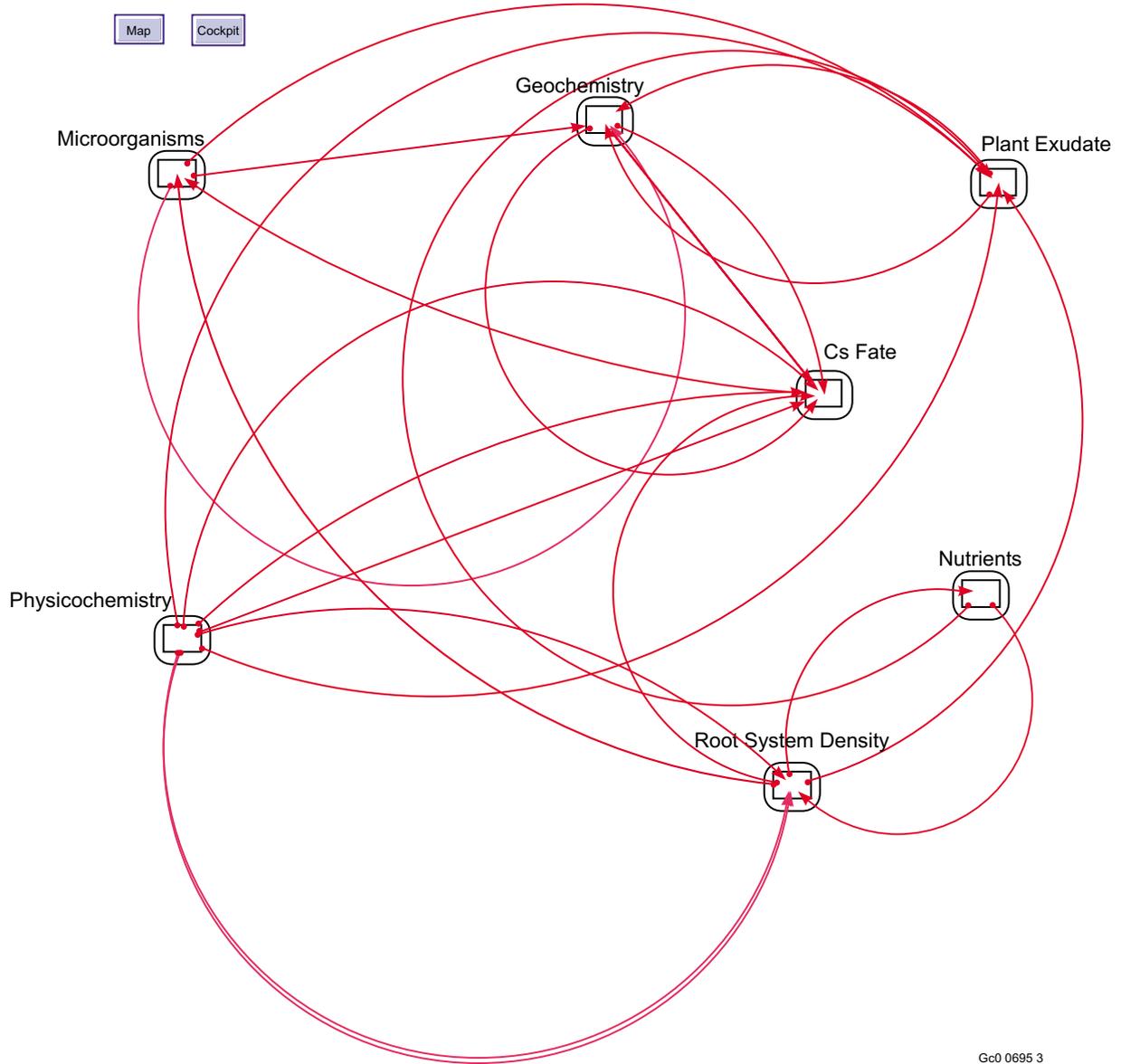


Figure 8. Model level of Stella software, indicating the Cs Fate sector and the six sectors affecting it.

Equilibrium controls the transfer between C_a and C_w . The model assumes a Langmuir type adsorption isotherm, such that:

$$C_{S_w} = \frac{\rho_b}{\theta^* conv} \frac{S_{max} K C_{S_a}}{1 + K C_{S_a}} \quad (2)$$

Where:

S_{max} = the maximum concentration of sites (e.g., $\mu\text{mol Cs/kg soil}$)

K = Langmuir adsorption parameter (1/aqueous concentration, e.g., L pore fluid/ $\mu\text{mol Cs}$)

ρ_b = dry bulk density of the soil (e.g., kg soil/ m^3 bulk soil)

θ = volumetric water content (e.g., m^3 pore fluid/ m^3 bulk soil)

conv = volumetric conversion (e.g., 1,000 L/ m^3)

The term $\rho_b/(\theta*\text{conv})$ translates the units of C_{s_w} from concentration per mass into a pore fluid volumetric concentration.

The derivative with respect to time of the mass balance equation is given as:

$$\frac{\partial C_{s_{total}}}{\partial t} = \frac{\partial C_{s_a}}{\partial t} + \frac{\partial C_{s_w}}{\partial t} + \frac{\partial C_{s_i}}{\partial t} + \frac{\partial C_{s_p}}{\partial t} \quad (3)$$

Following from the chain rule:

$$\frac{\partial C_{s_{total}}}{\partial t} = \frac{\partial C_{s_a}}{\partial t} + \frac{\partial C_{s_w}}{\partial C_{s_a}} \frac{\partial C_{s_a}}{\partial t} + \frac{\partial C_{s_i}}{\partial t} + \frac{\partial C_{s_p}}{\partial t} \quad (4)$$

The total mass of Cs per volume remains constant with time, i.e., the derivative with respect to time equals zero. The release of Cs from the bound phase to the soluble phase is calculated by assuming a simplified condition in which the change with respect to time of C_{s_p} equals zero.

$$\frac{\partial C_{s_a}}{\partial t} + \frac{\partial C_{s_w}}{\partial C_{s_a}} \frac{\partial C_{s_a}}{\partial t} + \frac{\partial C_{s_i}}{\partial t} = 0 \quad (5)$$

Therefore:

$$-\frac{\partial C_{s_a}}{\partial t} = \frac{\frac{\partial C_{s_i}}{\partial t}}{\left(1 + \frac{\partial C_{s_w}}{\partial C_{s_a}}\right)} \quad (6)$$

The derivative of the isotherm is calculated as:

$$\frac{\partial C_w}{\partial C_a} = \frac{\rho_b}{\theta * \text{conv}} \frac{S_{\max} K}{(1 + K C_a)^2} \quad (7)$$

Characterize exudate production and fate

We have completed a more thorough review of research on the effects of plant exudates in the rhizosphere and previous modeling efforts on plant exudates.

Laboratory Assembly and Manipulation of a Simplified Rhizosphere System

The subcontract with the Utah State University (USU) Crop Physiology Laboratory has been in place since about August 15, 2000. The purpose of the work being done by USU is to develop an artificial rhizosphere environment with liquid and solid-phase hydroponic technologies to be used in examining crested wheatgrass exudate production. While this work will be performed in FY 2001, the following activities have been achieved in the short time the subcontract has been in place:

- A graduate student has been hired to work on the task
- Genotypes of crested wheatgrass have been selected and hydroponic systems for culturing those plants are under construction
- Extensive literature has been reviewed and detailed experimental plans for these studies have been completed.

Ops Integration

WAG 4 requested the assistance of the rhizosphere engineering team in determining vegetation uptake and Cs movement at the CFA-08 sewage treatment plant drainfield located at the Central Facilities Area (CFA). The milestones for this work were as follows:

1. Sample vegetation from three plant species found on the drainfield and on a control site, and sample the soil adjacent to the plants at each sample location. Analyze the samples for Cs-137, total elemental Cs, and extractable nitrates in the soil.
2. Perform a literature review relative to phytoremediation of Cs at the INEEL.
3. Compile the results of the sample collection and analysis and the literature review and present the information at a Decision Analysis Forum for WAG 4 where the current Record of Decision (ROD) for the site was being reconsidered.
4. Participate as a voting member at the Decision Analysis Forum for WAG 4, where it was determined that there was sufficient data to merit a reconsideration of the current ROD for CFA-08.
5. Prepare a final report of the characterization results and literature review.
6. Publish a paper on the CFA-08 findings.

Results

The milestone for sample collection and analysis was met with the following findings:

- All of the plants (crested wheatgrass, sagebrush, and rabbit brush) accumulated detectable levels of Cs-137.
- Cs-137 was found to be accumulating at significant levels in the roots of crested wheatgrass on the CFA-08 drainfield.
- Elemental Cs was found at about 3 ppm on both the control site and the CFA-08 drainfield.

- Cs-137 did not contribute to the overall elemental Cs concentration.
- Cs is migrating upward in the soil. This upward mobility is assumed to be a result of vegetation creating an upward hydraulic gradient.
- A major issue and concern that had developed within the rhizosphere project was the amount of training required to conduct the field research. This training consumed not only a significant amount of the budget, but also caused fieldwork to be delayed due to the time it required. However, being able to leverage our scientific knowledge in support of Operations problems within WAGs not only provides us with additional field experience and opportunities to learn more about the rhizosphere, but it also shows the significance and potential benefit of our rhizosphere project in support of Environmental Management problems and issues at INEEL and elsewhere.

REFERENCES

1. R. C. Bartholomay, L. L. Knowbel, and L. C. Davis, "Mineralogy and Grain Size of Surficial Sediment from the Big Lost River Drainage and Vicinity, with Chemical and Physical Characteristics of Geologic Materials from Selected Sites at the Idaho National Engineering Laboratory, Idaho," *U.S. Geological Survey*, 1989, p. 74.
2. R. C. Bartholomay and L. L. Knobel, "Mineralogy and Grain Size of Surficial Sediment From the Little Lost River and Birch Creek Drainages, Idaho National Engineering Laboratory, Idaho," *U.S. Geological Survey*, 1989, p. 19.
3. R. C. Bartholomay, , "Mineralogical Correlation of Surficial Sediment From area Drainages with Selected Sedimentary Interbeds at the Idaho National Engineering Laboratory, Idaho," *U.S. Geological Survey*, 1990, p. 18.
4. G. L. Olson and D. J. Jeppson, "Idaho National Engineering Laboratory Soils Map," 1995.
5. C. T. Rightmire and B. D. Lewis, "Hydrogeology and Geochemistry of the Unsaturated Zone, Radioactive Waste Management Complex, Idaho National Engineering Laboratory, Idaho," *U.S. Geological Survey*, 1987, p 89,
6. R. O. Miller, J. Kotuby-Amacher, J. B. Rodriguez, "Western States Laboratory Proficiency Testing Program Soil and Plant Analytical Methods," Ver 4.10, 1998; from R. G. Gavlak, D. A. Horneck, R. O. Miller, *Plant, Soil and Water Reference Methods for the Western Region*, WREP 125, 1994.
7. D. Smart, A. Ferro, K. Ritchie, and B. Bugbee, "On the Use of Antibiotics to Reduce Rhizoplane Microbial Populations in Root Physiology and Ecology Investigations." *Physiol. Plantarum*, Vol. 95, 1995, pp. 533–540.
8. A. J. M. Smucker, and A. E. Erickson, "An aseptic mist chamber system: A method for measuring root processes of peas," *Agron. J.*, Vol. 68. 1976, pp. 59–62.
9. E. Benizri, A. Courtade, and A. Guckert, "Fate of two microorganisms in maize simulated rhizosphere under hydroponic sterile conditions," *Soil Biol. Biochem.*, Vol. 27(1.), 1995, pp. 71–77.

10. V. Groleau-Renaud, S. Plantureux, and A. Guckert, "Influence of plant morphology on root exudation of maize subjected to mechanical impedance in hydroponic conditions," *Plant Soil*, Vol 201, 1998, pp. 231–329.
11. B. Bugbee and F. B. Salisbury, "An Evaluation of MES (2(N-Morpholino)Ethanesulfonic Acid) and Amberlite IRC-50 as pH Buffers for Nutrient Solution Studies," *J. Plant Nutr.*, Vol. 8, 1988, pp. 567–583.
12. T. Grotenhuis and B. Bugbee, "Super-Optimal CO₂ Reduces Seed Yield but Not Vegetative Growth in Wheat." *Crop Sci.*, Vol. 37, 1997, pp. 1215–1222.
13. O. Monje and B. Bugbee, "Adaptation to High CO₂ Concentration In an Optimal Environment: Radiation Capture, Canopy Quantum Yield, and Carbon Use Efficiency," *Plant, Cell, and Environment*, Vol. 21, 1998, pp. 315–324.

Investigation of Factors Influencing Cesium Mobility and Uptake In Plant/Soil Systems

Studying How Root-Soil Systems Take Up Heavy Metals

Melinda Hamilton, Richard Hess, Tom Ward, Greg White, Reed Hoskinson, and Larry Cook (INEEL); Bruce Bugbee (USU); Lori Siegel (Northeastern)

SUMMARY

The heavy metal cesium is a common soil contaminant at DOE sites. While initial EM efforts to use plants to remove cesium and other metals from soils have been promising, fundamental understanding of how plants do this is lacking. This research will examine interactions within the root zone, or rhizosphere, that enable the uptake and storage of cesium in the plant. Remediation of metal and mixed-waste contaminated soils depends on the fundamental understanding of these processes. This task will improve long term stewardship by improving the long-term performance of ground cover over waste sites. Results of this task will also provide information to improve the modeling of the fate and transport of such contaminants through the soil.

The purpose of this task is to develop a sufficient understanding of rhizosphere processes to allow for prediction, modeling, and ultimately the control of contaminants in the rhizosphere. This is accomplished by focusing on biogeochemical processes that affect the mobility and bioavailability of metals in the rhizosphere. The rhizosphere can be viewed as the window to the vadose zone. The knowledge gained will lead to the development of cost-effective technologies for remediation of dispersed radionuclide/heavy metal and mixed waste contaminated soil, both in vegetated surface soil and subsurface soil. It is intended that the information obtained from this task will be combined with the ecological and biological understanding of the rhizosphere gained from the Ecological Engineering of Rhizosphere Systems task to develop a comprehensive understanding of the fate of Cs (cesium) in the rhizosphere. Many of the activities in this task, such as site selection, field characterization, and model development, are leveraging activities from the Ecological Engineering of Rhizosphere Systems task.

The variety of users that will benefit from low capital and operating cost ecosystem-based technologies include: DOE, Department of Defense, mining industry, oil and gas industry, and U.S. Department of Agriculture. This effort will advance ecological engineering technologies that are unique, competitive, and address pressing environmental problems or demands.

The current focus of this task on Cs bioavailability directly supports the Idaho Site Technology Coordination Group's Need Statement ID-6.2.08, which expresses a need for understanding the mechanisms that control Cs binding and the need for removal technologies. Cs contamination is the number one contaminant (by number of sites) both at the INEEL and across the DOE complex. At INEEL alone, there are more than 25 soil plumes known to have Cs contamination.

Selection of the parameters to be considered initially in the field characterization and conceptual modeling tasks has been completed. A database of literature has been compiled. Based on findings from the literature review, data from previous studies conducted here at the INEEL, and vegetation/soil Cs concentration data available from INEEL sites, we have identified biogeochemical parameters to be measured in the crested wheatgrass system.

TASK DESCRIPTION

The general objective of this research is to investigate, at molecular and atomic scales, the specific biogeochemical processes occurring in plant soil systems that are necessary to engineer remediation technologies. Environmental remediation applications for metal and mixed-waste contaminated soils that depend on the fundamental understanding of these processes will be the driver for this research. Because metal bioavailability is a key factor in successfully developing biological remediation technologies, the initial research objective for this task consists of developing the capability to understand and predict fate and transport of metals in plant/soil systems.

The work scope for this task includes two research elements considered imperative to developing an understanding of plant/soil ecology sufficient to allow engineering of plant/soil remediation technologies. These are rhizosphere biology—a molecular approach to plant and microbial genetics, biochemistry, and physiology—and geochemistry—an atomic approach to rhizosphere soil chemistry and physics. Studies on rhizosphere biology and geochemistry focus on the biological and geochemical phenomenon that greatly affect Cs bioavailability in the rhizosphere of the crested wheatgrass ecosystem at the INEEL. These studies consist of laboratory investigations focused on:

- Characterizing the quantity of plant root exudates and the quality of these exudates with respect to metal bioavailability
- Characterizing the quantity and quality of rhizosphere bacterial secreted Cs chelators
- Determining how Cs is bound to reactive mineral phases in soils at the INEEL and elsewhere
- Combining the biological and geochemical phenomenon to determine the rate of Cs and potassium, which is chemically similar to Cs, released from reference clays in the absences and presence of key components of plant exudates and microbial chelators.

This approach combines scientific investigations on biogeochemical rhizosphere mechanism affecting metal bioavailability with the ecological and biological understanding of rhizosphere gained from the Ecological Engineering of Rhizosphere Systems task to develop a more comprehensive understanding of fate of Cs in the rhizosphere.

Characterization of Crested Wheatgrass Root Exudates

The objective of this work is to identify root exudates from crested wheatgrass and quantify the effect of environmental factors on the production of exudates. Root exudates are typically comprised of low-molecular-weight compounds including organic acids, sugars, phenols, and amino acids. The quantity and quality of these compounds have a significant effect on microbial activity in the rhizosphere and are important in the function of the plant/soil system. Some of these compounds can increase the mobility and bioavailability of metals such as Cs from contaminated soils.

Under a subcontract with the INEEL, the Utah State University (USU) Crop Physiology Laboratory is performing experiments on crested wheatgrass using sterile root-zone environments. Solutions collected from these model systems are being analyzed to characterize root exudates. The amount and composition of these exudates is expected to vary with the type and amount of plant stress. Consequently, USU is examining the effects of nutrient, water, and oxygen stresses. They will manipulate these conditions in hydroponic/sterile media model systems (developed under the Ecological Engineering of Rhizosphere Systems task) to determine conditions that promote production of exudates. The information

obtained in this study is crucial to helping INEEL operations and DOE estimate contaminant migration from the shallow soil system, quantify the bioavailability of metal contaminants, and evaluate potential strategies for remediating metals-contaminated soil. The specific studies involved in this task include:

- Experiments to recover and measure the quantity and quality of root exudates of select genotypes of crested wheatgrass in sterile hydroponic systems
- Experiments to measure the quantity and quality of root exudates as a function of plant stress, including nutrient availability (particularly K⁺⁺), nitrogen form, root-zone water potential, root-zone oxygen availability, and plant age
- Experiments to quantify the effect of microorganisms on the net rhizosphere production of organic compounds by comparing inoculated and sterile plant cultures.

Crested Wheatgrass Root Exudates Sterile Hydroponic Systems

“Hycrest” crested wheatgrass has been used by researchers at USU in phytoremediation studies,¹ but a new cultivar of crested wheatgrass (CD-II) is more vigorous and stress resistant than “Hycrest.” Kay Asay and colleagues at the U.S. Department of Agriculture, Agricultural Research Service facility on the USU campus developed the CD-II cultivar. CD-II is PVP protected, but six companies have licenses to sell it, and seed is available in quantity.

Using these cultivars, the quantity and quality of root exudate of healthy (nonstressed) hydroponically grown crested wheatgrass plants is being studied at different stages of plant development. These studies are designed to determine the effect of physiological and morphological stages of plant growth and development during which exudate production occurs. To determine which factors have the greatest effect on exudate production, exudate production is being determined on the basis of total plant biomass, root biomass, and root density.

Exudates accumulate in the sterile hydroponic solution, but many exudates are too dilute for direct measurement. To address this challenge, aliquots of hydroponic solution will be concentrated on selective ion-exchange columns, which will then be desorbed and analyzed. These techniques expand on previously used techniques for the collection and analysis of trace amounts of trichloroethylene in plant/hydroponic systems.^{2,3}

Initially, the exudate analysis is focusing on the identification and quantification of acids because of their importance in metal complexation (oxalic acid, and citric acid). The secretion of low molecular weight organic acids contributes to the acidification of the rhizosphere and possibly the formation of soluble metal complexes. Mono-, di-, tri-, and hydroxycarboxylic acids have been reported as root exudates. Volatile low molecular weight monocarboxylic acids are often analyzed by gas chromatography (GC) without derivation. Di- and tri-carboxylic acids have been analyzed by GC after derivation (methylation),⁴ but have also been analyzed by high-performance liquid chromatography (HPLC)⁵ and ion chromatographic (IC) procedures.⁶ Concentration of the carboxylic acids prior to instrumental analysis has been accomplished by a variety of solid sorbent techniques, including anion exchange resins and acidification/nonpolar solvent extraction. After developing methods for the acids, phenolics, and flavonones may be examined. Like the acids, phenolics have been analyzed by GC and HPLC after a solid phase concentration step. HPLC has become the analytical method of choice for flavonones.⁷

Root Exudates As a Function of Plant Stress

Root-zone stress damages membranes and it is generally thought that stress increases the rate of exudation from roots. These studies are examining the effect of three types of stress on exudate quantity and composition. Potassium stress is of particular interest because of its chemical similarity to Cs. Potassium stress is imposed in hydroponic culture by adding potassium at 10 and 50% of the concentration of the control. USU's previous experience indicates that these levels are sufficient to impose mild and severe potassium stress. Nutrient imbalances caused by excess potassium are rare and thus high levels of potassium are not being studied in these initial tests. A Cs toxicity/stress treatment is also being examined using nonradioactive CsCl_2 (available from Sigma Chemical Co.). The Cs concentration in hydroponic solution will be determined based on the naturally occurring Cs levels in the contaminated soils at sites of interest to the INEEL, which we have determined to be about 3 mg/kg.

The form of nitrogen available at the root surface determines rhizosphere pH and may significantly influence the efflux and type of exudates. Nitrogen represents over 80% of the ions absorbed by plant roots. All plant cells must maintain charge balance with the external solution. When nitrate is absorbed an OH^- ion is excreted, when ammonium is absorbed a H^+ ion is excreted. The rhizosphere pH can be up to 2 pH units above or below the bulk soil pH because of the effect of differential forms of nitrogen absorption. Nitrogen form can be manipulated in the field and can be readily manipulated in hydroponics.

Root-zone oxygen availability can vary considerably in the field. Anaerobic conditions have a significant effect on the integrity of root membranes.⁸ The effect of oxygen availability in the root zone will be studied by turning off the flow of air to the root-zone in hydroponic culture. The oxygen in solution is depleted within a few hours and the resulting change in exudate efflux can be determined.

Root zone water potential will be studied using solid porous media. Polyethylene glycol has been used to impose water stress in hydroponic culture, but plants can take up even high molecular weight polyethylene glycol compounds and cause reduced abnormal growth. Additionally, the polyethylene glycol in solution may interfere with the analysis of exudates in the solution. Given that a hydroponic system can be developed that will allow the effective manipulation of root zone water potential for the purpose of studying exudate production, exudates resulting from mild and severe water stress will be measured by eluting the organic compounds from the media.

Effect of Microorganisms On the Net Efflux of Organic Compounds

To determine the net efflux of organic compounds as affected by microorganisms, the hydroponic culture vessels will be inoculated with the prominent bacteria found in INEEL crested wheatgrass community soils. We anticipate using pseudomonas- and pseudomonad-like bacteria as of this writing, but the final selection will be determined by the characterization studies of the Ecological Engineering of Rhizosphere Systems task. Our experience with inoculation of hydroponic cultures suggests that the inoculation is much more effective if the microorganisms are cultured on a solid substrate, such as a diatomaceous earth, and the solid substrate is then added to the liquid hydroponic vessel.

Characterization of Cesium Chelators Secreted by Bacteria

The purpose of this research is to determine whether bacteria present in the rhizosphere secrete compounds that affect the solubility and mobility of Cs and potentially other metals by chelating/binding those metals. To search for such compounds, bacteria will be grown in a minimal salts medium—medium B, which we have been using for plating rhizosphere samples—with a neutral (nonmetal-binding) carbon and energy source, such as glucose or glycerol. After growth, all the bacteria will be removed by a combination of centrifugation (10 min. at 5,000 rpm) followed by filtration of the

supernatant through a 0.2 μm filter. The cell-free supernatant will be analyzed by HPLC on a column (Brownlee Polypore H, 10 μm particle size) designed to separate small organic acids. Any nonmedium-derived peaks present in the chromatogram will be identified, by elution time if possible, and then subjected to mass spectrometry for either confirmation or initial identification. This supernatant will then be analyzed for binding to Cs as described below.

The bacteria to be evaluated in these experiments will be several individual isolates from INEEL rhizosphere samples collected from the Ecological Engineering of Rhizosphere Systems task, task studies, and consortia derived from those rhizosphere samples. The use of mixed populations allows the testing of many individual bacteria in the same experiment, but requires isolation of the responsible individual strain if a positive result is observed for the mixed culture. In addition, consortia have a greater probability of degrading organic molecules that are secreted, thus leading to false negative results.

The above experiments will then be repeated, with the modification of growing the bacteria in the presence of Cs, using only bacterial strains previously found to be producing potentially chelating compounds. For these experiments the potassium concentration in the minimal medium will be reduced. The organic molecules in the cell free supernatant will again be analyzed by HPLC, and the chromatographic pattern will be compared to that produced in the absence of Cs. Peaks showing significant changes (newly appearing, significantly increased or decreased) will be identified. The compounds in this supernatant will then be analyzed for Cs binding activity as for the non-Cs-treated supernatant using the various assays described below. The difference for these analyses will be that the Cs will have to be removed from the supernatant, probably an ion exchange chromatography method, before analysis of chelator activity. For both potential chelator preparations (+Cs) the activity of the total supernatant will be assayed first. If activity is observed, the various peaks separated by HPLC will be individually analyzed to identify the components possessing Cs binding activity.

Several types of assays will be initially investigated to determine which is best for analyzing Cs binding capability. One type is a spectrophotometric assay in which a complex possessing a well defined spectrum is formed between Cs and a known chelator. An aliquot of the sample containing potential chelator(s) is added, and if the Cs is removed from its complex with the known chelator by any components of the sample, the spectrum of the complex will change. A second type of experiment is a chromatographic or electrophoretic shift experiment, in which the mobility of Cs is analyzed in the presence and absence of the potential chelator. Binding of Cs by a chelating molecule in the sample will alter the mobility of the Cs ions under such analytical conditions. A third type of experiment makes use of nuclear magnetic resonance (NMR). When potential chelators have been identified (see above), the NMR spectra of these organic molecules can be analyzed in the absence and presence of Cs. If the organic molecule significantly interacts with the Cs ion, the NMR spectrum of the organic molecule will change.

Characterization of Cs Binding to Soils

The purpose of this work is to examine how Cs is bound to reactive mineral phases in soils at the INEEL and elsewhere. In some INEEL soils, Cs is very tightly bound and has proven almost impossible to remove from soil particles except by complete particle dissolution. There is some belief that Cs, as well as other contaminant metals, can become incorporated into the structure of reactive mineral phases; however, it is more probable that contaminants are strongly bound to minerals in some very tight manner. The latter concept has not been proven or demonstrated on INEEL soils. The strong association with certain mineral types, primarily highly charged 2:1 phyllosilicates, is thought to be by intercalation and fixation. The latter process may be due to replacement of potassium in the crystalline matrix of the

mineral. For these studies, the Savannah River Ecology Laboratory, operated by the University of Georgia, is:

- Characterizing mineral and organic constituents of soils from the INEEL and elsewhere, and determining their associated physicochemical properties
- Determining the association of Cs with reactive mineral phases in soils
- Determining the primary mineral phases controlling Cs sorption in soils
- Investigating Cs short-term sorption/desorption mechanisms in soils.

The characterization phase of the study will involve complete chemical and mineralogical analyses of the selected soils. The physical, chemical, and mineralogical characterization of the sediments will be conducted following well established methods^{9,10} and will include particle size analysis, organic carbon, exchangeable cations, cation exchange capacity, pH, x-ray diffraction, and thermal analysis of the clay fraction. The fractionated sediments will also be examined by scanning and transmission electron microscopies, and synchrotron x-ray fluorescence (XRF) spectroscopy to provide detailed information on the important Cs sorbent phases, and on Cs distribution in the selected soils. The synchrotron XRF microprobe on beamlines X-26A at the National Synchrotron Light Source (Brookhaven National Laboratory, NY) and Sector 13 at the Advanced Photon Source (Argonne National Laboratory) will be used for micro-SXRF (soft XRF) and XAFS (x-ray absorption fine structure) in their normal configuration with the addition of a silicon, channel-cut (111) monochromator on the incident radiation. The beam will be focused to ~1 μm using Kirkpatrick-Baez double elliptical mirrors. Measurements at the Cs L_{III} edge will also be collected in the fluorescence mode using a filter/Soller slit configuration at beamline X23B at the National Synchrotron Light Source (NSLS) facility. A custom-manufactured 10- μm (0.4-mil) thick Sc foil filter (Rhone-Poulenc, Phoenix, Arizona) combined with Soller slits will be used to reduce the large background signal due to scattered radiation from the samples. The use of the Sc foil filter has been shown to increase the signal-to-background ratio by an approximate factor of 6.¹¹ The space encompassing the x-ray beam path after the ionization chamber that monitors the incident x-ray intensity (I_0), the space between the sample and the ionization chamber monitoring the fluorescent radiation intensity, and the chamber space surrounding the sample, will be filled with free-flowing He gas to further reduce the effects of scattering from the air.

The desorption/leachability of Cs from soils will be evaluated in both batch and column experiments. The batch experiments will be conducted following the methods outlined in References 12 and 13. The samples will be transferred to a stirred water-jacketed reaction flask under a N_2 atmosphere. The pH and ionic strength of a degassed soil solution suspension will be adjusted with N_2 -purged NaOH or HClO_4 and competing cation (Ca^{2+} , K^+ , NH_4^+) additions, and allowed to equilibrate prior to sampling suspension aliquots.

The column experiments will be conducted following the methods of Anderson et al.,¹⁴ where 25×2.5 cm columns will be leached at a constant Darcy velocity of 1.3 cm hr^{-1} with a HPLC pump. Leaching solutions will be selected for a limited range of ionic strength and pH values by examination of the batch sorption data. Column effluents will be collected in a fraction collector and filtered effluents analyzed as outlined below.

Samples will be reacted with solutions of varying ionic strength (0.01, 0.1, and 1 M both Ca- and K- ClO_4) and pH (3, 6, and 8). Cs and major cation (Ca, Mg, K, Na) concentrations in filtrates from the incubation and extraction procedures (0.1 μm polycarbonate filter) will be determined by ICP-MS (inductively coupled plasma mass spectrometry) analysis. Sulfate, NO_3^- , and PO_4^{3-} analyses will be

conducted by ion chromatography. Dissolved organic carbon will be determined on the filtrates using a Shimadzu TOC-500 Organic Carbon Analyzer.

The bonding environment of Cs in mineral phases in INEEL soils will also be evaluated through a selective extraction procedure which partitions Cs to exchangeable planar sites (1 M CaCl₂), interlayer selective sites (1 M NH₄Cl), and fixed Cs (residual). The Cs partitioned to these various pools will be examined prior to and following desorption/leachability studies and prior to and following organic matter and Fe-oxides.

Relationships will be developed between mineralogical characterization, ion exchange selectivity, Cs bonding environments, and Cs distributions between planar, selective, and fixed sorption sites.

Cesium Uptake and Release by Phyllosilicates

The purpose of this work is to quantify the rate of binding and release of Cs⁺ from phyllosilicates commonly found at INEEL and DOE sites. This work plan is based on the hypothesis that the release of Cs⁺ in the rhizosphere is controlled by diffusion from the interlayers of phyllosilicates. Cs⁺ occurs in a readily exchangeable form that is bioavailable (planar surfaces of phyllosilicates, Fe- and Al-hydroxides, organic matter) and a more recalcitrant form bound in the interlayers of phyllosilicate minerals common in soils (mica, illite, vermiculite, smectite). The rate of exchange of Cs⁺ from the interlayers of the phyllosilicates by other ions with low hydration energies (e.g. K⁺) is controlled by diffusion of ions in the interlayers. In a closed system, we expect the amount of Cs⁺ bound to the exchangeable sites to decrease over time, and the concentration of Cs⁺ in the “fixed” interlayer sites to increase. When plants are K⁺ limited, exudate production increases. Root exudates are typically comprised of low-molecular-weight compounds including organic acids, sugars, phenols, and amino acids. The organic acids, attack (weather) the phyllosilicates, by breaking down the octahedral layers and releasing K⁺ and consequently Cs⁺ from the interlayers. The rate of release of “fixed” K⁺ and Cs⁺ from phyllosilicates by weathering reactions driven by plant exudates is expected to be greater than the rate of release by diffusion. At the INEEL site, those phyllosilicates are most likely, mica, illite, and interlayered illite/smectite clay. This work, conducted under the supervision of Dr. Carl D. Palmer at the INEEL, includes:

- Reviewing the literature on Cs⁺ binding and release from soils and specific soil components including minerals, amorphous oxides, and organic matter
- Developing mathematical models for the long-term uptake and release of Cs⁺ by ideal clay structures
- Performing long-term uptake and release studies of Cs⁺ by reference clays
- Measuring the rate of release of Cs⁺ and K⁺ by reference clays in the presence of model compounds representative of key components of plant exudates (e.g., specific organic acids).

Subtask 1 is essential to the task and will be initiated immediately. Subtasks 2 and 3 complement one another. Although Subtask 2 will be initiated before Subtask 3, results from experimental work in Subtask 3 will feed back into the modeling effort in Subtask 2. These subtasks will rely on input from Dr. Bertschs work to insure that the clay materials are good choices and that the conceptual model is consistent with field observations. The mathematical model will be used to quantify the migration of the Cs⁺ from the recalcitrant pool to the more bioavailable pools in the Stella model. The experimental work in Subtask 3, does not involve the use of any plant or microbial exudates, and it will serve as the control experiments for the plant exudate-clay interaction work in Subtask 4. This subtask will require input from

the plant exudate work by Dr. Bugbee at USU and by Tom Ward at the INEEL to insure that the organic acids and other exudates that we use in these experiments are reasonable choices.

Literature Review On Cs⁺ Binding and Release From Soils

There is extensive literature on Cs⁺ binding to different soil materials. It is essential that we review these papers and summarize this literature in a general review. This review will help to insure that we do not overlook important processes affecting Cs⁺ binding in the rhizosphere.

Mathematical Models for the Long-Term Uptake and Release of Cs⁺

The release of the “fixed” K⁺ from soils and minerals has been considered a diffusion-controlled process.^{15,16} Since both K⁺ and Cs⁺ have low hydration energies, we suspect that the behavior of these two ions will be similar. Several mathematical models of K⁺ release from soils have been proposed¹⁷⁻²¹ and may be applicable to Cs⁺ uptake and release. Simple analytical solutions for diffusion in rectangular regions and parallelepipeds^{22,23} can be adapted; however, there are several potential limitations to these solutions. For example, collapse of the interlayer thickness can occur when monovalent ions with low hydration energies substitute in the interlayer. The interlayer thickness depends on the concentration of the substituting ion, consequently, the interlayer diffusion coefficient may also be concentration dependent. The boundary conditions for many applications may be more complex than constant concentration (Dirichlet type boundary condition), constant flux (Neuman type boundary condition), or a linear mass transfer boundary (“radiation” type boundary condition). The jumps in the concentration versus time data observed by Comans and Hockley²⁴ clearly suggests that more than one process is involved in the binding of Cs⁺ even in monomineral systems. Indeed, they propose a four box model that includes an instantaneous equilibrium process, a kinetically reversible process, and an irreversible kinetic process. Based on our literature review, we will propose several mathematical models for Cs⁺ binding in monomineral systems. These solutions may be either analytical or numerical. The actual equations we use will depend on the appropriate boundary conditions and other processes that are operating in the experiments we will be conducting and in the field situations that are likely to be encountered. It is important for us to link the aqueous concentration to the concentration at the boundary of the particle. If the diffusion coefficients are concentration dependent or there are too many complexities, it may be simpler to use a numerical solution. We will adjust our approach following the literature review and we will modify our models as experimental data become available.

Long-Term Uptake and Release Studies of Cs⁺ By Reference Clays

Reference phyllosilicates (illite, smectite, interlayered illite/smectite) will be obtained through various sources including the Clay Minerals Society. The samples will be pretreated to remove carbonates (1 M NaOAc at pH 5), organic matter (H₂O₂), and iron oxides (sodium dithionite-citrate).²⁵ The clays will then be sieved to remove any coarse materials and then dispersed using ultrasonics. A relatively narrow range of grain size will be obtained by sedimentation of this dispersed suspension. The samples will then be washed three times with a 1 M solution of NaCl. The materials will then be washed with ultra-pure (>14 MΩ cm) water until the AgNO₃ test for Cl⁻ is negative. The clays will then be stored in a refrigerator as a suspension until needed.

An aliquot of the suspension will be filtered and dried in a desiccator over a saturated CaCl₂ solution (relative humidity ~30%). The materials will then be characterized by powder x-ray diffraction, simultaneous thermal analysis, and Fourier infrared spectroscopy. Brunauer, Emmett, Teller (BET) surface areas will be obtained for each size fraction and reference clay. Samples of the clay will be viewed using electron microscopy (scanning and transmission electron microscopies) to measure the relative dimensions of the clay particles. Chemical composition will be obtained by XRF. The ammonium

acetate method^{26,27} will be used to obtain exchangeable cations and cation exchange capacities. Grain-size distribution will be obtained by photon correlation spectroscopy.

Batch adsorption experiments will be conducted by spiking suspensions of the mineral material with CsCl and KCl. At least three concentrations will be used for each salt. The aqueous concentrations of the salts and the solid:solution ratios to be used in the experiment will be estimated from literature review and from the modeling. Our initial estimate of the particle concentration is 100 mg L⁻¹. Salt concentrations will likely range from 1 to 1,000 μM. The experiments will be conducted near-neutral pH. Although we suspect that the nonspecific binding will be pH dependent, the specific binding occurring in the interlayers is less likely to be pH dependent. For Cs sorption on illite, only minor variations in K_d with pH have been observed.²⁸ Cs⁺ and K⁺ concentrations will be measured using ICP-MS.

Samples for the release experiments will be prepared by placing the clay in a 1 M solution of CsCl and KCl at 85°C for at least 3 months. The time scale will be better estimated based on the modeling and literature review. The samples will then be washed with ultrapure water until the AgNO₃ test is negative. The suspension will then be filtered and the filter cake air-dried until needed.

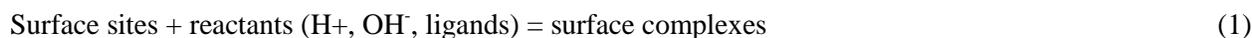
The release experiments will be conducted as flow-through experiments to keep the aqueous concentrations low, thereby increasing the gradient near the boundary and decreasing the time for completion of the experiment.

Samples of the clay at different times during the release experiment will be analyzed by powder x-ray diffraction and x-ray absorption spectroscopy. This aspect of the subtask should be done in cooperation with Paul M. Bertsch at the University of Georgia.

Rate of Release of Cs⁺ and K⁺ by Reference Clays in the Presence of Key Components of Plant Exudates

Plants can affect the weathering rates of minerals through both physical and chemical processes.²⁹ Physical processes include physical disintegration of bedrock material, changes in soil permeability, evapotranspiration, and binding and retention of soil particles. We will focus on the more direct chemical effects, which include lowering pH by CO₂ generated by root and microbial respiration, and lowering pH by adding organic acids and introducing organic chelates from plant roots and microbes. To understand how these chemical processes can increase the bioavailability of Cs in the rhizosphere, we must understand the weathering of silicate minerals, primarily, the phyllosilicates that are known to bind Cs⁺.

In general, rates of oxide and silicate mineral dissolution are known to be fairly constant at circum-neutral pH and to increase in both acidic and alkaline solutions. In addition, the rate of dissolution can also be increased by the presence of organic ligands. The dissolution of minerals is believed to involve two key steps.³⁰ In the first step, surface species are formed via the following formula:



This process has been shown to be relatively fast and reversible, hence it can be described as an equilibrium reaction. The second key process is the detachment of the metal ion from the surface into solution as follows:



This detachment process is the rate-limiting step and the surface complex is the precursor of the activated complex (see Reference 30). Thus, the rate of ligand-promoted dissolution, r_L , is proportional to the activity of the surface species as follows:

$$r_L = k'_L [L]_S \quad (3)$$

where $[L]_S$ denotes the concentration of the surface complex.

Proton- and hydroxyl-promoted dissolution requires coordination of several ions around the metal ion. The rates of proton- and hydroxyl-promoted dissolution, r_H and r_{OH} , are given as:

$$r_H = k'_H [H^+]_S^j \quad (4)$$

and

$$r_{OH} = k'_{OH} [OH^-]_S^i \quad (5)$$

where:

The exponents j and i correspond to the valance of the coordinated metal ion, $[H^+]_S^j$ is the concentration of protonated surface hydroxy groups in excess of the zero point charge and $[OH^-]_S^i$ is the concentration of deprotonated surface groups in excess of the zero point charge. The overall rate of dissolution of the mineral, is therefore given by:

$$r = k'_H [H^+]_S^j + k'_{H_2O} + k'_{OH^-} [OH^-]_S^i + k'_L [L]_S \quad (6)$$

where the term $k'H_2O$ refers to a zero-order process to describe the circumneutral pH region where the rate of dissolution is independent of pH.²⁹

The rate given in Equation (6) was developed for simple oxides. Nonetheless, the general concepts presented should also apply to more complex silicates. A key difference when considering the dissolution of phyllosilicates, such as kaolinite and muscovite, is that the tetrahedral layers are relatively nonreactive. Dissolution is controlled by the detachment of Al, which is primarily in the octahedral layer of the phyllosilicates. Therefore, reactions are going to occur at the edges of the crystallites where the octahedral layers are exposed to the solution.

We will conduct experiments to measure the ligand-promoted release of K^+ and Cs^+ from reference clays. The reference clays saturated with CsCl and KCl solutions in Subtask 3 will also be used in experiments to measure the release of Cs^+ and K^+ in the presence of key components of plant exudates. We will focus on organic acids and most likely, aliphatic and aromatic dicarboxylic acids that have been demonstrated to strongly bind metal ions. The specific acids that will be used will be based on the plant exudate work being done at USU. Experiments will be conducted in the presence of a 0.1 M NaCl solution. A control experiment containing no organic acids will also be conducted. $HClO_4$ will be used to adjust the pH of the control experiment to be identical to that of the experiments with organic acid. All solutions will be prepared using ultrapure water ($>14 \text{ M}\Omega\text{-cm}$). Water will be purged for at least 10 minutes with N_2 bubbled through 0.1 m NaOH to remove CO_2 . All solutions will be prepared in a glove box equipped with a CO_2 scrubber. Experiments will be conducted in high-density polyethylene bottles. These bottles will be sealed in glass canning jars before they are removed from the glove box. All materials will be sterilized prior to use to eliminate potential biological activity in the reaction vessels.

Because the rate of weathering of the phyllosilicates is proportional to the adsorbed ligand concentration, it is necessary to determine the amount of adsorbed ligand in the experiments. The adsorbed ligand concentration is a function of the total ligand concentration, pH, the acid/base properties of the absorbent, and total surface area of the absorbent. The acid/base properties of the clays will be measured by potentiometric titration with at least three different ionic strengths using an autotitrator. Specific surface areas will be obtained in Subtask 3.

Experiments will be conducted using clay suspensions in 0.1 M NaCl solutions. Time-series of concentrations will be obtained to test proposed kinetic models for the release of K^+ and Cs^+ in the presence of organic chelating agents. Experiments will be conducted at various pH (4, 5, 6, 7, 8, and 9) and ligand concentrations. At this time, we propose using ligand concentrations of 0.01, 0.03, 0.1, 0.3, and 1.0 mM; however, the final decision will be based on results of plant exudate studies at Idaho State University (ISU). The pH will be kept constant by periodically adjusting the pH with $HClO_4$ and NaOH. The suspensions will be prepared in high-density polyethylene (HDPE) bottles in the glove box, sealed in canning jars, removed from the chamber, and placed in a shaking constant temperature bath set at 25°C. The jars will be returned to the glove box for periodic sampling. Aliquots of each sample will be filtered through a 0.4- μm filter. A portion of this sample will be used to measure pH. A second portion will be acidified with nitric acid for subsequent analysis by atomic absorption spectroscopy and ICP-MS. A third portion of the sample will be saved as a nonacidified sample for Si and organic ligand analysis. Na, K, Cs, and Al concentrations will be measured on the acidified samples by a combination of atomic absorption spectrophotometry and ICP-MS. Si concentrations will be measured colorimetrically using an ammonium molybdate method (ASTM D 859-94). Ligand concentration will be measured by ion chromatography.

In a second series of experiments, the model clays will be subjected to dissolution at a fixed ligand concentration and pH, but with the particle concentration (the clay concentration) at five different values. A third set of experiments will be conducted with a fixed particle concentration, a fixed ligand concentration, and a fixed pH, but on three different size fractions of the clay.

Samples of the reacted clay material will be characterized by powder x-ray diffraction, thermogravimetry, and x-ray absorption spectroscopy.

These studies will provide a rate equation for the release of Cs^+ and K^+ in the presence of pertinent organic ligands.

ACCOMPLISHMENTS

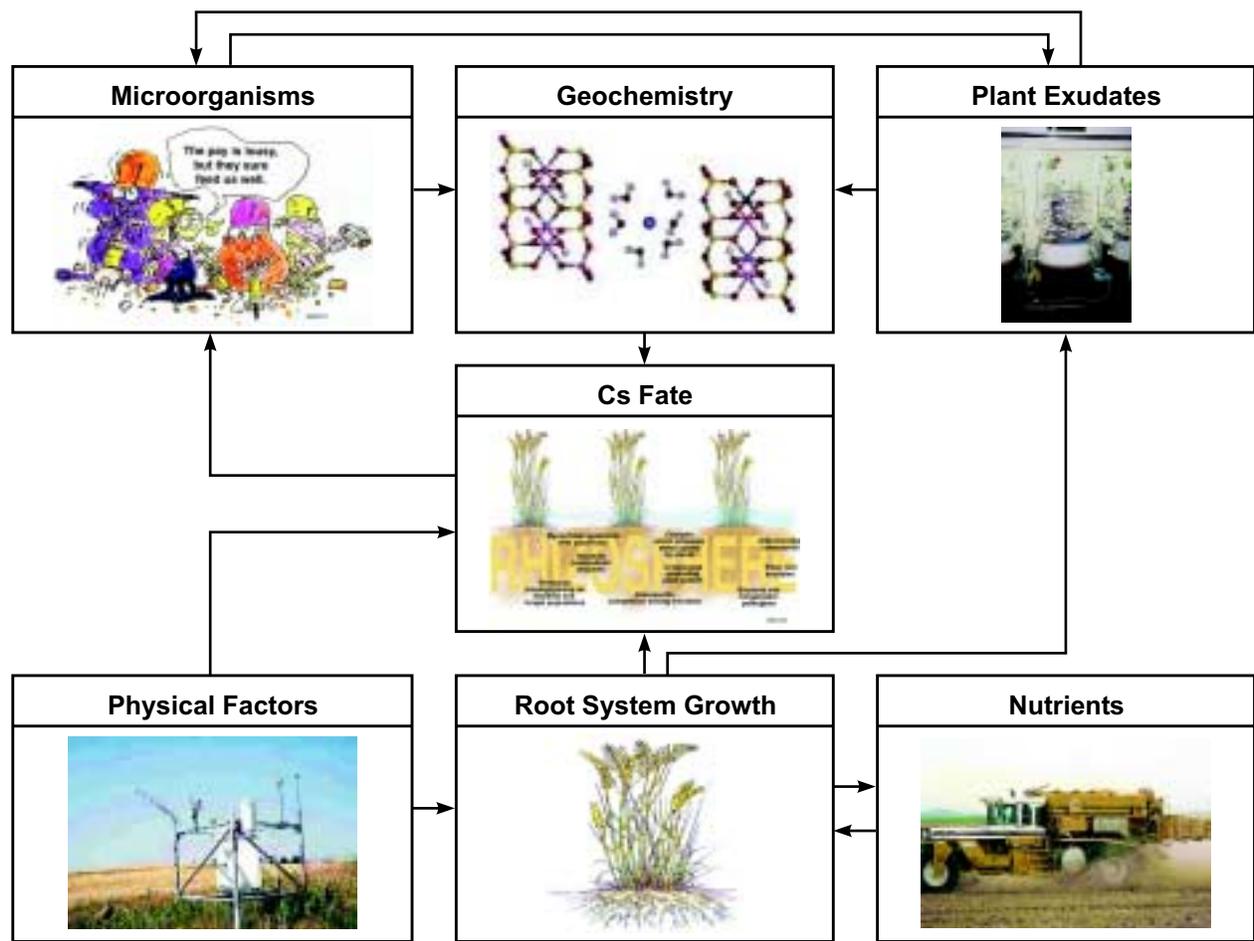
Selection of the parameters to be considered initially in the field characterization and conceptual modeling subtasks has been completed. A database of literature has been compiled. Based on findings from the literature review, data from previous studies conducted here at the INEEL, and vegetation/soil Cs concentration data available from INEEL sites, we have identified biogeochemical parameters to be measured in the crested wheatgrass system. The sampling and analysis to be conducted in the field characterization studies are included in the Ecological Engineering of Rhizosphere Systems task report, which explains that field site selection has been completed and field characterization (including geochemical parameter characterization) has been initiated.

The parameters being evaluated are included in the preliminary conceptual model. The modeling effort is being implemented using Systems Thinking, integrating the relationships between the many factors affecting Cs solubilization. To date, we have established the basic associations using software.

Stella/iThink modeling software is based on this approach. The software allows us to set up these relationships in sectors with each sector representing a submodel. We have established many of the basic

relationships within each submodel, as well as the interactions between submodels. This approach allows for expertise in defining each sector, while simultaneously promoting the ecological packet. The model setup still requires refinement, with a few elements and the interactions between elements still to be incorporated. Data will be incorporated into the model as it is obtained. Refinement of the geochemical submodel (Cs binding to soil) and integration of the Cs binding submodel with the ecological and biological submodels is being conducted as part of this task (see Figure 1).

The purpose of the work being done by USU is to examine how crested wheatgrass exudate production is affected by environmental/nutrient induced plant stress, microbes, and plant growth and development. Genotypes of crested wheatgrass have been selected and hydroponics systems for culturing those plants are under construction. Extensive literature review and detailed experimental plans for these studies have been completed.



Gc01 0002

Figure 1. Stella/iThink modeling software interface level showing the Cs Fate sector (center box) and the six sectors (or submodels) affecting it.

A literature review of Cs binding in soils has been initiated. Based on this literature review we have developed a hypothesis concerning the uptake and release of Cs by phyllosilicates in the rhizosphere. Based on a review of studies of the mineralogy at the INEEL site, we have tentatively identified illite, Ca-smectite, interlayered illite/smectite, and mica as the most likely phyllosilicates at the our field site. We have acquired reference illite and smectite clays for our experimental work.

REFERENCES

1. A. Ferro, R. Simms, and B. Bugbee, "Hycrest Crested Wheatgrass Accelerates the Degradation of Pentachlorophenol in Soil," *Journal, Environmental Quality*, Vol. 23, 1994, pp. 272–279.
2. B. J. Orchard, W. J. Doucette, J. K. Chard, and B. Bugbee, "Uptake of Trichloroethylene by Hybrid Poplar Trees Grown Hydroponically in High Rate, Flow-Through Plant Growth Chambers," *Environmental Toxicology and Chemistry*, Vol. 19, 2000, pp. 895–903.
3. B. J. Orchard, , W. J. Doucette, J. K. Chard, and B. Bugbee. "A Novel Laboratory System For Determining the Fate of Trichloroethylene In Plants." *Environmental Toxicology and Chemistry*, Vol. 19, 2000, pp. 888–894.
4. A. Szmigielska, K. Van Rees, et al., "Determination of Low Molecular Weight Dicarboxylic Acids in Root Exudates by Gas Chromatography," *Journal, Agriculture Food Chemistry*, Vol. 43, 1995, pp. 956–959.
5. R. McFeeters, "Single Injection HPLC Analysis of Acids, Sugars and Alcohols in Cucumber Fermentations," *Journal of Agriculture and Food Chemistry*, Vol. 41, 1993, pp. 1439–1443.
6. B. Lilieholm, L. Dudley, et al., "Oxalate Determination In Soils Using Ion Chromatography," *Soil Science Society of America Proceedings*, Vol. 56, 1992, pp. 324–326.
7. H. Merken and G. Beecher, "Measurement of Food Flavonoids by High-Performance Liquid Chromatography: A Review," *Journal of Agricultural and Food Chemistry*, Vol. 48(3), 2000, pp. 577–599.
8. H. Marschner, *Mineral Nutrition of Higher Plants*, 2nd Edition, 1995, Academic Press, NY, p. 889.
9. M. L. Jackson, *Soil Chemical Analysis-Advanced Course*, 2nd ed. Pub. by author, Dept. of Soils, University of WI, Madison, WI. M. L. Jackson, Madison, WI, 1979.
10. F. W. Kunze and J. B. Dixon, "Pretreatment for Mineralogical Analysis," *In A. Klute (ed.) Methods of soil analysis, Part 1, 2nd ed. Agron. Monogr.*, Vol. 9, ASA and SSSA, Madison, WI, 1986.
11. K. M. Kemner, D. B. Hunter, W. T. Elam, and P. M. Bertsch, "XAFS Studies of Solution Phase Complexes of Cesium with Dibenzo-18-crown-6 Ethers," *Journal of Physical Chemistry*, Vol. 100, 1996, pp.11698–11703.
12. Calvin C. Ainswoth, James L. Pilon, Paul L. Gassman, and William G, Van Der Sluys, "Cobalt, Cadmium, and Lead Sorption to Hydrous Iron Oxide: Residence Time Effect," *Soil Sci. Soc. Amer. J.*, Vol. 58, 1994, pp. 1615–1623.
13. J. P. McKinley, J. M. Zachara, S. C. Smith, and G. D. Turner, "The Influence of Uranyl Hydrolysis and Multiple Site-binding Reactions on Adsorption of U (VI) to Montmorillonite," *Clays Clay Mineral.*, Vol 43, 1995, pp 586–598.
14. M. A. Anderson, P. M. Bertsch, S. B. Feldman, and L. W. Zelazny, "Interactions of acidic metal-rich coal pile runoff with a subsoil," *Environ. Sci. Technol.*, Vol. 25, 1991, pp. 2038–2046.

15. S. Feigenbaum, R. Edelstein, and I. Shainberg, "Release Rate of K and Structural Cations From Mica to Ion Exchangers in Dilute Solutions," *Soil Science Society of America Proceedings*, Vol. 45, 1981, pp. 501–506.
16. H. W. Martin and D. L. Sparks, "Kinetics of Nonexchangeable Potassium Release From Two Coastal Plain Soils," *Soil Science Society of America Journal*, Vol. 47, 1983, pp. 883–887.
17. M. G. Reed and A. D. Scott, "Kinetics of Potassium Release From Biotite and Muscovite in Sodium Tetraphenylboron Solution," *Soil Science Society of America Proceedings*, Vol. 26, 1962, pp. 437–440.
18. M. M. Mortland and B. Ellis, "Kinetics of Potassium Release From Biotite," *Soil Science Society of America Proceedings*, Vol. 22, 1959a, pp. 503–508.
19. M. M. Mortland and B. Ellis, "Release of Fixed Potassium as a Diffusion Controlled Process," *Soil Science Society of America Proceedings*, Vol. 23, 1959b, pp. 363–364.
20. Quirk J. P. and J. H. Chute, "Potassium Release From Mica-Like Clay Minerals," *Transactions of the 9th International Congress of Soil Science*, 1968, pp. 671–681.
21. J. A. Rausell-Colom, T. R. Sweatman, C. B. Wells, and K. Norrish, "Studies in the Artificial Weathering of Mica," *In Experimental Pedology* (ed. E. G. Hallsworth and D. V. Crawford), Butterworths, 1965, pp. 40–72.
22. H. S. Carslaw and J. C. Jaegar, *Conduction of Heat in Solids*, Oxford University Press, 1959.
23. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, 1975.
24. R. N. J. Comans and D. E. Hockley, "Kinetics of Cesium Sorption on Illite," *Geochimica et Cosmochimica Acta*, Vol. 56, 1992, pp. 1157–1164.
25. G. W. Gee and J. W. Bauder, "Particle-Size Analysis," *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*, Vol. 9 (ed. A. Klute), 1986, pp. 383–411, American Society of Agronomy, Inc. and Soil Science Society of America, Inc.
26. J. D. Rhoades, "Cation Exchange Capacity," *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*, Vol. 9 (ed. A. L. Page, R. H. Miller, and D. R. Keeney), 1982, pp. 149–157. American Society of Agronomy, Inc. and Soil Science Society of America, Inc.
27. G. W. Thomas, "Exchangeable Cations," *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*, Vol. 9 (ed. A. L. Page, R. H. Miller, and D. R. Keeney), 1982, pp. 159–165. American Society of Agronomy, Inc., and Soil Science Society of America, Inc.
28. C. Poinssot, B. Bayens, and M. H. Bradbury, "Experimental and Modeling Studies of Cesium Sorption on Illite," *Geochimica et Cosmochimica Acta*, Vol. 63(19/20), 1999, pp. 3217–3227.
29. J. I. Drever, "The Effect of Land Plants On Weathering Rates of Silicate Minerals," *Geochimica et Cosmochimica Acta*, Vol. 58(10), 1994, pp. 2325–2332.
30. W. Stumm and E. Wieland, "Dissolution of Oxide and Silicate Minerals: Rates Depend on Surface Speciation" *Aquatic Chemical Kinetics* (ed. W. Stumm), John Wiley & Sons, Inc., 1990, pp. 367–400.

Long-term Biogeochemical Destruction and Control of Aquifer Contaminants Using Single-Well Push-Pull Tests

Controlling and Destroying Aquifer Contaminants in Place

**Rick S. Colwell, Yoshiko Fujita, Mark Delwiche, JoAnna Taylor (INEEL);
Jonathan Istok (Oregon State University)**

SUMMARY

This task involves the use single-well push-pull tests^a to evaluate induced and natural biogeochemical processes in the fractured rock aquifer in INEEL wells that are representative of conditions where important metal or trichloroethylene (TCE) plumes exist. The results from these tests will improve understanding of subsurface biogeochemical transformations aimed at developing approaches for controlling and destroying dissolved contaminants in aquifers. This task integrates a successful Environmental Management Science Program (EMSP) project at Oregon State University into INEEL capabilities. In general, the push-pull approach to characterizing in situ microbial activities is a low-cost monitoring tool that can develop a better understanding of the long-term fate and transport of contamination in subsurface environments. This task is relevant to EM's mission because it addresses critical questions in the area of biogeochemical transformations. For specific applications, this task will determine how the biology, chemistry, and geology of the subsurface interact to control contaminant fate and transport and determine subsurface remediation approaches.

The push-pull tests will include additions of urea to the Snake River Plain aquifer to increase calcite precipitation in the aquifer and the coprecipitation of divalent metals such as strontium. Once formed, mineral calcite is stable under normal conditions in arid western aquifers because coprecipitated radio-nuclides are held within the mineral matrix as they undergo radioactive half-life decay. This solution is engineered to permanently control residual radionuclide contamination left in place until the radioactive hazard has decayed to safe levels. A second push-pull test is planned that will evaluate in situ methano-trophy (a process that can degrade TCE) to provide estimates of the inherent rate of aerobic natural attenuation of TCE (TCE has a 16-year half-life) in the aquifer. In areas where TCE is broadly distributed in a diffuse plume, such as in the aquifer at Test Area North (TAN) on the INEEL, there is evidence that such degradation is already occurring. This portion of the study will determine the inherent rates of a specific microbial process that can degrade TCE and has been implicated in natural attenuation. Data derived from this study will contribute to fate and transport modeling to support long-term stewardship.

Our FY 2000 activities centered on preparing for Tasks 1 and 2, which will be completed in FY 2001. These activities included researching and identifying candidate wells for the push-pull tests, developing a sampling plan for the wells of interest, and verifying urea detection limits at concentrations consistent with those planned for the push-pull test (100 to 2,500 μM). We determined that Snake River Plain aquifer isolates may require additional carbon if increases in urea hydrolysis are expected.

a. A push-pull test consists of the injection of a prepared test solution into the aquifer (push) followed by a rest phase and then an extraction of the test solution/groundwater mixture from the same well (pull). During the extraction phase, samples are collected to analyze for injected solutes and reaction products to prepare breakthrough curves and to calculate mass balances and reaction kinetics.

TASK DESCRIPTION

This task involves the use of single-well push-pull tests to evaluate induced biogeochemical processes in a fractured rock aquifer (see Figures 1 and 2). This is accomplished by determining the response of aquifer microbial communities to the introduction of urea (Subtask 1), which is microbially-hydrolyzed, leading to an increase in aquifer pH and consequent increase in calcite precipitation rate; and ^{13}C -labeled methane (Subtask 2) as a way of assessing the indigenous rates of methanotrophic (microbial methane utilization) activity in an aquifer. Both of these subtasks are distinct from but related to ongoing EM-funded efforts aimed at developing approaches for dealing with dissolved contaminants in aquifers (Smith et al. "Calcite Precipitation and Trace Metals Partitioning in Groundwater and the Vadose Zone," FY 2000 through FY 2002; Colwell et al. "Control of Biologically Active Degradation Zones by Vertical Heterogeneity," FY 1996 through FY 2000; Istok et al., "In Situ, Field-Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well, Push-Pull Test," FY 1996 through FY 2000).

FY 2000 Activities

In preparation to perform Tasks 1 and 2 (in FY 2001), we have selected three wells (USGS-025, P&W-1 and P&W-3). These wells are 5 miles northwest of TAN in an uncontaminated section of the Snake River Plain aquifer. They have conditions approximating those found in the aquifer at TAN, but without the restrictions associated with sampling within the RCRA-controlled TCE plume. P&W-1 has a high transmissivity ($2.5 \times 10^5 \text{ ft}^2/\text{day}$), indicating that at that location the aquifer is capable of transmitting high amounts of water to regional wells. By comparison, wells in the Snake River Plain aquifer range in transmissivities from $1.1 \text{ ft}^2/\text{day}$ to $7.6 \times 10^5 \text{ ft}^2/\text{day}$. Water chemistries for the wells indicate that the aquifer in this location is characteristic of the Snake River Plain aquifer at large (high dissolved oxygen, ca. 13°C , low dissolved organic carbon, and ca. $45 \text{ Ca}^{+2} \text{ mg/L}$).

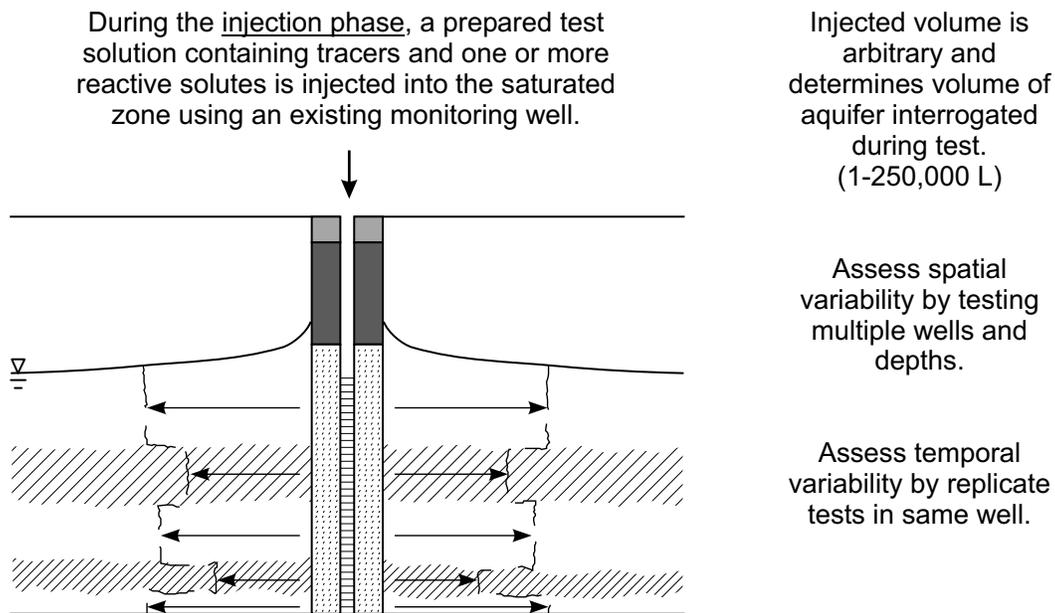


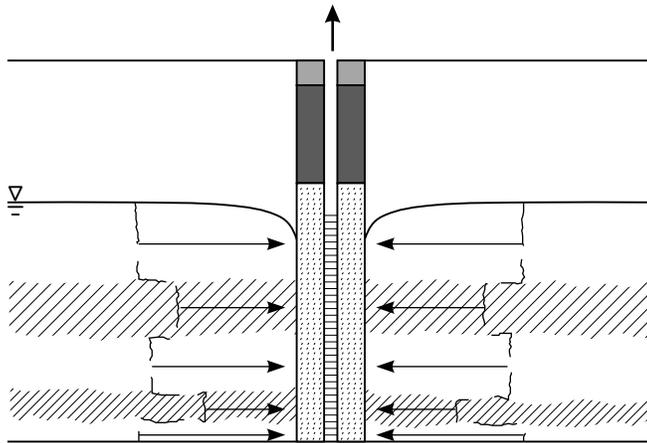
Figure 1. Depiction of injection phase of push-pull test.

During the extraction phase, flow is reversed and samples of test solution/groundwater mixture are collected and analyzed to develop breakthrough curves for injected tracer and reactants, and potential reaction products formed *in situ*.

Accurate mass balances are easily computed.

Flow reversal reduces effects of heterogeneities on breakthrough curves.

Ability to recover injected reagents simplifies regulatory approval for injecting exotic materials.



Gc00 0696 2

Figure 2. Depiction of extraction phase of push-pull test.

Our lab experiments focused on adjusting our capabilities for working with model urea hydrolyzers (e.g., *Bacillus pasteurii*) under idealized laboratory conditions to working with environmental isolates from the Snake River Plain aquifer under conditions that more closely reflect those in the aquifer. The best approach for measuring urea concentrations in groundwater removed during the “pull” phase of the field studies has been determined. The selected method for urea detection is based on a reaction of primary amine (urea) with p-dimethylaminobenzaldehyde (DMAB) to form a colored product (Schiff base). The assay was found to be linear between urea concentrations of 100 to 2,500 μM . The use of this assay is favored in addition to measurements of aquifer pH and ammonia because it provides a direct indication of the fate of the urea that will be introduced to the aquifer. Other lab work pointed to the possibility that a carbon source will need to be added along with the urea during the push-pull experiments. Preliminary results indicated that while *Bacillus pasteurii* can degrade urea without an additional carbon source being added, selected isolates from the Snake River Plain aquifer cannot. Microorganisms 9Bb-1 and 110AD from the aquifer were able to degrade urea only when a carbon source was added to the samples. The field work associated with this task is will be started as soon as permitting allows use of the identified wells.

FY 2001 Activities

For Subtask 1 (in situ urea hydrolysis), 250 L of water containing a bromide tracer (~100 mM) and urea (~300 mM) will be injected into the Snake River Plain aquifer at a specific depth interval in the selected well. This urea concentration has been used in laboratory experiments to study calcite precipitation by known urea-hydrolyzing bacteria. After a rest period with no pumping, ground-water will be extracted from the same location and analyzed for urea, ammonia, calcium, strontium, pH, total microbial cells, bacteria capable of hydrolyzing urea (urease-positive cells), and changes in the kinetics of microbial urea hydrolysis. We expect that stimulation of indigenous microbial urease activity will cause urea to decrease while ammonia increases. The pH should increase and dissolved calcium and strontium should decrease as calcite is precipitated from the water. We should observe an increase in numbers of both total cells and urease positive cells, and the kinetics of urea hydrolysis should change such that

following the addition of urea, communities exhibit a higher maximal rate of urea hydrolysis (V_{max}) and a lower affinity for the substrate (K_m).

For Subtask 2 (methanotrophy), ^{13}C -labeled methane will be added to the aquifer to achieve concentrations consistent with natural methane concentrations found therein (nM to μM levels). Following the “push” of ^{13}C -labeled methane into the wells and the subsequent resting phase, water withdrawn from the well will be analyzed for ^{13}C -labeled methane, ^{13}C -labeled carbon dioxide, total cell numbers, and methanotrophs. Microbial phospholipid fatty acids (PLFA) will be analyzed by Microbial Insights (Knoxville, Tennessee) and will indicate changes in the total biomass and microbial community structure as a result of the treatment. Because PLFA analysis is performed with a mass spectrometer, we will also be able to determine which components of the microbial community incorporate the ^{13}C -labeled carbon into their cellular lipids. In this experiment, we expect that in situ methanotrophic activity will cause ^{13}C -labeled methane to decrease during the resting period following injection while ^{13}C -labeled carbon dioxide will increase. If the levels of ^{13}C -labeled methane that are added are truly equivalent to the background levels of methane, then total cell numbers and methanotrophs should not increase markedly. Mass spectrometer analysis of samples obtained after the resting period should indicate that the ^{13}C -label is present in the membrane lipids of methanotrophs. This task is will be started in spring 2001.

For both tasks, control experiments will be conducted before adding the urea or methane, wherein unamended water will be added to determine the effects of the injection on the system, estimate the hydraulic gradient, and evaluate the background concentrations of key analytes. An important aspect of this work is the ability to obtain in situ estimates for microbial activity, expressed as a rate of injected substrate consumption and/or product formation, including potentially the determination of Michaelis-Menton kinetic parameters for each process.

ACCOMPLISHMENTS

Our accomplishment during FY 2000 are as follows:

- We researched and identified candidate wells for the push-pull tests
- We developed a sampling plan for the wells of interest
- We verified urea detection limits at concentrations consistent with those planned for the push-pull test (100 to 2,500 μM).
- We determined that Snake River Plain aquifer isolates may require additional carbon if increases in urea hydrolysis are expected.

REFERENCES

None

Unified Hydrogeophysical Parameter Estimation Approach to Subsurface Contaminant Transport— Subsurface Imaging Collaboration with the Center for Subsurface Sensing and Imaging Systems

Integrating Cross-Discipline Data to Image the Subsurface

Earl D. Mattson (INEEL); Eric Miller and Mohammed Khames (CenSSIS)

SUMMARY

The complexity of subsurface science and the cleanup issues currently faced by EM can only be addressed by integrating research from different scientific disciplines into cohesive models. Too often, geophysical, hydrological, contaminant transport, and geochemical data are collected and analyzed independently from one another.

A major barrier to incorporating geophysical characterization techniques to subsurface contaminant transport predictions is nonintegration of the multiple disciplines involved. Too often, geophysical, hydrological, forward transport model, and geochemical data are collected and analyzed independently of one another, resulting in disjointed data interpretation and analysis. Our research suggests a unified approach to integrate geophysical tomography with hydrological state variable data to better describe the flow and transport parameters in the subsurface. This research will focus on using quantitative optimization tools to integrate geophysical and hydrological data for imaging the subsurface. This should lead to better understanding of the functional inter-relatedness between specific geophysical and hydrogeophysical parameters, and ultimately contribute to more accurate subsurface modeling. This proposed approach would better constrain the tomographic inversion techniques for imaging the subsurface and develop functional relationships between geophysical electrical resistivity signals and hydrogeophysical parameters.

This work is a collaboration of the INEEL Geoscience Department and the National Science Foundation's (NSF's) Center for SubSurface Imaging Systems (CenSSIS) at Northeastern University. CenSSIS is a new NSF center, with expertise in quantitative optimization tools to invert geophysical signal data to geophysical parameters. The advantage of using subsurface geophysical signals to characterize the vadose zone is the ability to measure between boreholes in multiple dimensions. The INEEL has expertise with vadose zone measurement techniques and field and laboratory experimental design. These measurement techniques allow continuous measurement of contaminant transport variables but lack the advantage of multidimensionality. Combining the strengths of CenSSIS's geophysical inversion techniques and the INEEL's soil physics instrumentation will better constrain the geophysical inverse solution. Subsequently, this methodology will allow better prediction of contaminant transport through the vadose zone.

TASK DESCRIPTION

Mineral exploration has incorporated surface direct current (dc) resistivity methods since the 1880s in the search for mineral deposits. More recently, electrical methods have been adapted to obtain physical properties of groundwater and vadose zone materials. These properties include porosity, water saturation, temperature, pore water ionic concentration, and the presence of clay minerals.

Beginning in the 1980s, dc resistivity surveys were modified by placing electrodes into boreholes rather than solely on the surface. Collecting data through this multidimensional electrode layout and by analyzing the data with inversion algorithms, researchers could obtain detailed maps of the resistivity distribution between a set of boreholes. This innovation is called electrical resistance tomography (ERT). ERT was successfully used in several studies to monitor soil saturation (e.g., Daily et al.¹), temperature during infiltration experiments at air injection (e.g., Lundegard and Labrecque²), and thermal remediation sites (e.g., Ramirez et al.³).

ERT data are collected by transmitting a constant current through a pair of electrodes while measuring the resultant voltage potentials between all possible receiving-electrode pairs. A second pair of electrodes is then selected to transmit the electrical current while measuring the voltage potential field. This process is repeated until every possible pair of electrodes is being used as transmitters and receivers (see Figure 1).

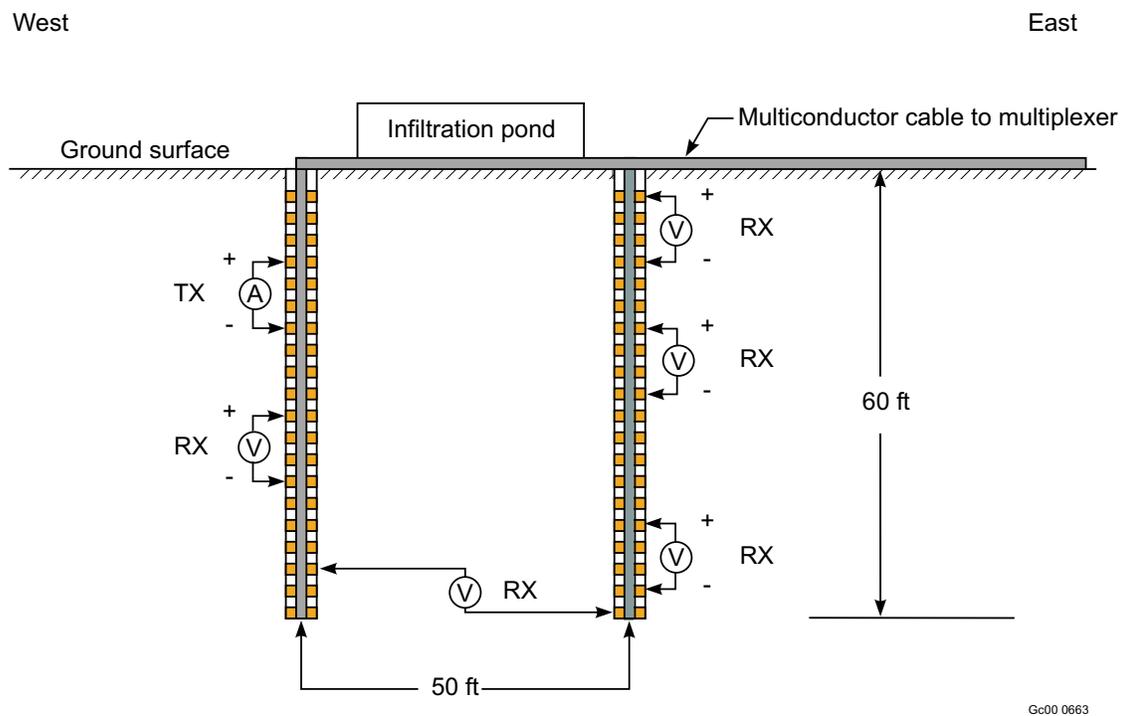


Figure 1. Hypothetical example of electrical resistivity tomography data acquisition between two boreholes in the subsurface.

Typically, a tomographic or inverse scattering type of imaging approach is used to convert ERT data into a 3-D volumetric rendering of the subsurface, space-varying electrical resistance. However, this image formation problem is highly ill-posed. Sensor noise and other unmodeled effects can cause the resulting renderings to possess nonphysical artifacts, making them practically useless.⁴ A common method used in an effort to overcome this difficulty is to examine temporal differences of the electrical tomographic images in an effort to detect anthropogenic electrical conductivity changes. Although this method should detect any changes in the tomographic image, the change cannot be quantitatively described. A method for overcoming such difficulties is to incorporate constraints into the processing scheme to quantify the real electrical conductivity. The method we propose draws on CenSSIS's previous work in this area (e.g., level set and other geometric imaging methods), in addition to incorporating constraints through the point measurements described above.

Our general approach is to explore using level set methods for anomaly characterization coupled with low-order models for describing the background structure. Level sets have proved very useful in the image processing community as a tool for automatically and robustly locating objects of unknown geometry in a scene. Moreover, there have been some very promising theoretical results in the past few years on the use and application of level-set methods for tomographic inverse problems like ERT, but at radar frequencies. One drawback of a level-set approach is that it typically requires rather detailed knowledge of the background in which the object is embedded. Moreover, it is typically assumed that the objects of interest have the same contrast against the background and that this contrast is known. Finally, level sets are most often implemented in 2-D problems. For the ERT problem of interest, none of these assumptions is valid, so we seek to extend and modify the basic level-set approach to address these issues by performing the following subtasks:

1. Develop models that relate electrical properties of the subsurface to hydrological properties. Such models are necessary to allow us to translate the information from the electrical sensors into a form relevant to the data provided by the hydrological instruments. Equations under consideration are those provided by Rhoades et al.⁵ and Mualum and Friedman.⁶
2. Develop multiscale imaging methods for reconciling the differing scales over which the data provide information. The issue is how one employs point data taken from a sample in a borehole to constrain the value of the hydrological state variables at positions far into the formation. Roughly speaking we seek a mathematical technique for the spatial propagation these point constraints.
3. Implement the resulting algorithms for 3-D problems.
4. Evaluate on both synthetic and actual field data.

The goal of this task is to develop and validate advanced tomographic image formation and object detection techniques for sensing subsurface structure via ERT.

ACCOMPLISHMENTS

This task has two phases. Phase 1 (FY 2000) runs from May 1, 2000 through September 30, 2000. During this period, we have initiated appropriate cooperative agreements between INEEL and CenSSIS, started incorporating a forward model into the inversion model, and considered appropriate field sites for subsequent demonstration. Most of the research will take place during Phase 2 (FY 2001), which will involve collecting data, developing numerical algorithms, and analyzing data. We expect to advance theory as we develop algorithms and incorporate it into forward numerical models, and we will conduct experimental analysis of electrical properties of soils and their relationship to unsaturated hydrogeologic variables. We will develop experimental data sets to evaluate the inversion technique and submit an abstract to a national conference (e.g., American Geophysical Union, Fall 2001) describing results.

We acquired a 3-D forward modeling code for the task and obtained a finite difference modeling code⁷ for simulating an ERT system. This code has been compiled and validated using the included test cases on the computer system at CenSSIS.

We obtained partial equipment needed for the ERT data collection. We located a Hach terrameter at the INEEL and evaluated it for its appropriateness to measure soil core electrical conductivity and for adapting it to measure the electrical conductivity in situ using the electrical conductivity probe manufactured by Geoprobe Inc. The ERT data acquisition equipment is being pursued through separate funding.

We have proposed a field site and are currently evaluating it for its potential to demonstrate the effectiveness of the approach. The site consists of eolian dune sand overlying fractured basalt. Hydrologic characterization of this site indicates that the overlying sand consists of numerous layers of fine sand to silt material.

This 1-1/2-year collaborative research effort will result in better constrained 3-D tomographic inversion techniques for imaging the subsurface. This technique will allow better characterization and monitoring of the vadose zone and will ultimately result in more accurate prediction of contaminant transport through vadose zone soils.

REFERENCES

1. Daily et al. 1992, "Electrical Resistivity Tomography of Vadose Zone Water Movement," *Water Resources Research*, Vol. 28, No. 5, pp.1429–1442.
2. P. D. Lundegard and D. LaBrecque, 1995. "Air Sparging in a Sandy Aquifer (Florence, Oregon, U.S.A.): Actual and Apparent Radius of Influence," *Journal of Contaminant Hydrology*, Vol. 19, pp. 1–27.
3. A. Ramirez, 1993, "Monitoring an Underground Steam Injection Process Using Electrical Resistance Tomography," *Water Resources Research*, Vol. 29, No. 1, p. 73 –87.
4. D. Labrecque, et al., 1996, "The Effects of Noise on Occam's Inversion of Resistivity Tomography Data," *Geophysics*, Vol. 61, No. 2, pp. 538–548.
5. J. D. Rhoades, , et al., 1976, "Effects of Liquid-phase Electrical Conductivity, Water Content, and Surface Conductivity on Bulk Soil Electrical Conductivity," *Soil Science Society of America Journal*, Vol. 40, pp. 651–655.
6. Y. Mualem and S. P. Friedman, 1991, "Theoretical predication of electrical conductivity in saturated and unsaturated soil," *Water Resources Research*, Vol. 12, pp. 513 –522.
7. J. Zhang, A. Mackie, and T. Madden, 1995, "3-D Resistivity Forward Modeling and Inversion Using Conjugate Gradients," *Geophysics*, Vol. 60, pp. 1313–1325.

Innovative Approaches to Characterize Vadose Zone Hydraulic Properties

New Methods for Measuring Water Flow Through INEEL Subsurface Samples

David N. Thompson and Kristine E. Baker (INEEL); Clark Lindenmeier (PNNL)

SUMMARY

Current methods for characterizing soil hydraulics are time-consuming and unsuitable for routine monitoring. Yet soil hydraulics are key to understanding the fate and transport of contaminants and other molecules that interact with rocks, soils, and water in the subsurface. This research explores the application of a relatively new commercially available instrument—the unsaturated flow apparatus (UFA)—which promises to reduce the time (currently months) and cost required to measure hydraulic properties in subsurface samples. Use of the UFA to measure hydraulic properties can also improve the quality of the hydraulic data. Additionally, the UFA can also be used to determine microbial activities in vadose soil cores for in situ bioremediation, which is a major thrust of Environmental Management's (EM's) research and development. This research enables EM's mission and contributes to understanding the relationship between compact subsurface soils and water retention. Being able to predict hydraulic characteristics of the subsurface will support long-term stewardship with engineering solutions to predict and manage contaminants.

This novel application of UFA technology to compactible soils requires that we characterize the effects of centrifugal force on compaction of vadose zone sample cores. In collaboration with researchers at the Pacific Northwest National Laboratory (PNNL), we then use x-ray microtomography (XMT) to determine the relationship between changes in soil porosity and centrifugal force. The objectives of our work this year were to (a) obtain and install a UFA instrument at the INEEL, (b) establish collaboration with PNNL researchers, and (c) begin measuring soil hydraulic properties using traditional hanging columns/pressure cells to establish a baseline with which to compare porosity changes in UFA-measured cores. We purchased and installed the UFA instrument and are developing in-house expertise in its operation. Traditional methods for hydraulic characterization are underway, and the potential for applying XMT to characterizing the compaction looks promising.

TASK DESCRIPTION

Introduction

The INEEL recently embarked on a multiyear program to better understand the movement and transformation of reactive constituents in the subsurface. We regularly sample and characterize soil cores, most studies use hanging columns and pressure cells for the characterization, which is very time consuming. These hanging column measurements are often inaccurate owing to measurement of small weight differences in large samples. Thus, both the time required to do the analyses (weeks to months) and the method of obtaining the results should be improved to give more consistent and useful data.

A recent development in the field of hydrology of the Unsaturated Flow Apparatus, or UFA, addresses the time limitation. The UFA is a flow-through centrifuge device used to measure fluid transport properties of porous media. This is accomplished in hours to days by subjecting the sample to fluid driving forces up to 10,000 g. Steady state is reached within hours, even at very low hydraulic

conductivities, removing traditional time barriers. For example, UFA Ventures Inc. has estimated analysis time comparisons between the UFA method and baseline technologies¹ (see Table 1). Times estimated for traditional soil columns and curve-fitting estimations are from standard references to the techniques; times for the UFA method are from UFA Ventures' experience with the technique (see Reference 1). Note that no one has ever used traditional soil columns to measure hydraulic conductivities down to 10^{-10} cm/sec, but it is conservatively estimated to require over 20 years. Also, note that the baseline technologies cannot be used for certain applications.

Table 1. Estimated time savings for measuring hydraulic properties using the UFA method versus traditional soil columns and curve fitting (adapted from Reference 1).

New Methods for Measuring Water Flow through INEEL Subsurface Samples	Baseline Methods		
	Soil Columns	Curve Fitting	UFA Method
Unsaturated hydraulic conductivity of soils and other porous media:			
Water (saturated to 10^{-7} cm/s)	1 year	6 weeks	3 days
Water (saturated to 10^{-10} cm/s)	>20 years	3 months	5 days
Nonaqueous phase liquid e.g., CCl ₄ and oils (saturated to 10^{-10} cm/s)	>20 years	NP*	5 days
Unsaturated retardation experiments (e.g., uranium, assuming $R_f = 10$ at 20% of saturation)	1 month	NP*	1 week
Pristine pore water extraction from unsaturated soils, sludges, and other solids	NP*	NP*	1 day
Precision and accuracy at the very low water contents expected in the field at arid sites	Excellent	Fair	Excellent
Feasible number of samples to be investigated in a year per laboratory	20	20	2000

* NP = Not possible using this method.

There are many subsurface projects at the INEEL that could use the UFA instrument with undeformable core samples, and all would benefit from the rapid measurement capability. An ASTM method for using the instrument to measure hydraulic conductivities of undeformable rock cores, cement, sand, etc., was recently approved.² However, an important factor that limits the utility of the UFA for rapid measurement of hydraulic properties is the potential for compacting the samples under the applied centrifugal force. When the sample is an *undeformable* rock or cement core, this is not generally a problem, since the centrifuge cannot apply sufficient force to deform the core. Soil samples are compactible if they are composed of particulates not arranged in a close-packed structure or cemented. Any soil that is not cemented or that contains sufficient soil water will therefore be compactible, especially soils that contain clays (clays swell with added water). Thus, compaction of soil cores is expected in the UFA, which severely limits characterization of soils using the UFA.

Although use of the UFA with relatively undeformable rock or cement cores and noncompactible soils is standard, the UFA is thus not generally recommended for compactible samples.³ Indeed, the ASTM method above does not include compactible soils (see Reference 3). Still, it would be very helpful

to have a defensible way to use the UFA for compactible or marginally compactible samples for all the reasons noted above. Any routine measurement of soil core hydraulic properties (compared to rock cores) will require the user to account for the decreases in interstitial pore volume as the centrifugal force is increased. For example, consider a related and interfacing ESR task, “Reactive Transport in Variably Saturated Heterogeneous Media: Relationships Between Moisture Content, Tension, and Biogeochemical Activity in the Vadose Zone.” In this task, microbial activities are measured in a compactible vadose soil over a wide range of moisture contents. With a measured pore size distribution, the microbial activity is correlated with the amount of water in pores that are available to the microbes. For the results to be valid, the substrate must initially be homogeneously distributed throughout the soil water. This type of study has not previously been attempted due to the long times required to distribute the substrate solution throughout the soil water using traditional methods, since the substrate would be completely consumed in the days to months necessary to reach equilibrium. The UFA will be used to circumvent this time limitation—the soil is first saturated with dilute substrate solution and then quickly drained in the UFA to the desired water content. However, since the soil is compactible, the effects of the UFA on the pore volume distribution as the sample is drained must be quantified. If a mathematical relationship between applied centrifugal force and compaction (decreasing pore volume) can be derived and used to quantify the effects, it would help extend use of the UFA to this compactible soil, and to soils in general.

In light of the above, the broad objectives of this ESRC task are as follows:

- Purchase a UFA and use intact undeformable materials (rock and or sand) rather than compactible materials to gain expertise in using the instrument to be developed. The INEEL will do this in collaboration with researchers at the Pacific Northwest National Laboratory (PNNL), who have extensive experience in using the UFA.
- Determine the time to reach several steady state moisture contents on the characteristic drainage curve for intact cores of the compactible vadose soil used in the interfacing ESR task (vary the angular velocity).
- Compare moisture characteristic drainage curves measured for the compactible soil in the UFA with similar curves measured in hanging columns/pressure cells.
- Observe changes in the axial density of the intact soil cores before and after measurement in the UFA and in hanging columns/pressure cells, using x-ray microtomography. This will also be in collaboration with researchers at the PNNL.
- Quantify the changes in the relative porosity from the x-ray microtomography data using software. Pore volumes will also be estimated for comparison using nitrogen adsorption in parallel samples.
- Quantitatively relate the characteristic curve measured in the UFA to that measured in the hanging columns/pressure cells.

A single soil will give results specific to that soil. However, our intent is to determine whether a stress-strain-compaction model can be used to address the effects of compaction on a UFA-measured moisture characteristic curve. Such a relationship would offer a new tool for characterizing compressible soils in the UFA, and would answer specific questions of the interfacing ESR microbial activity task. Results from the single compactible soil from the interfacing task will allow us to assess this relationship.

A significant aspect of this task is our interaction with PNNL. Researchers at PNNL have been using the UFA to study DOE-relevant problems and so can assist us in quickly obtaining the expertise

needed to productively use this important new tool. In addition, the x-ray microtomography laboratory offers a unique way to study the effects of structure on hydraulic properties, which will be a valuable asset to subsurface research at the INEEL.

Background

Although the vadose zone is often relied on as the primary protective barrier to prevent groundwater contamination, it is often the conduit for transport of contamination from the surface to subsurface water supplies. Because our current understanding of the movement and transformation of contaminants is not adequate to accurately predict their behavior under unsaturated conditions, new coordinated research and technology development activities are needed for improved and sustainable stewardship of the vadose zone. Prediction of contaminant fate and transport in the vadose zone requires the ability to represent the important physical, biological, and geochemical processes and properties of vadose zone soils and sediments in a modeling framework that allows accurate assessment of the transport, retention, and transformation of contaminants and other solutes (nutrients, electron acceptor and or donors, etc.). Experimental investigations rely on current methods for obtaining the necessary data, which are both time-consuming and inherently inaccurate. These methods use hanging columns and pressure cells to estimate hydraulic properties of vadose samples.

The two most important parameters required to effectively describe subsurface transport and behavior are hydraulic conductivity and matrix potential. These parameters are strong, nonlinear functions of the volumetric water content. These functional relationships are controlled or influenced by the pore-size distribution which, in turn, is controlled or influenced by the grain-size distribution, density, and pore connectivity factor. For the vadose zone, hydraulic conductivity and matrix potential can be used in predictive modeling to determine travel times. The matrix potential can be determined using closed centrifugation, where no fluid enters the sample during rotation.^{4,5} The recently developed UFA can do this. The UFA is a flow-through centrifuge device used to measure the fluid transport properties of porous media, in hours to days. The UFA can be used to apply an adjustable acceleration to a core sample⁶ by subjecting the sample to fluid driving forces up to 10,000 g. To measure the matrix potential by this method, the sample is first saturated using an appropriate method. The sample is then placed in the UFA, and the angular velocity is stepwise increased from 300 to 10,000 rpm. At each angular velocity, the sample drains until the matrix potential is equal and opposite to the equivalent pressure of the acceleration. Steady state is reached within hours, even at very low hydraulic conductivities, removing the traditional time barrier to these types of experiments.

The principal difficulty in using the UFA is with soils that can swell or compact. The applied centrifugal force can compact the sample, and samples containing clays can swell within the UFA sample holder and limit flow through the lines leading to the top of the sample. The effect of this compaction is observable when UFA results are compared with results from hanging column experiments with the same soil, as shown in Figure 1. The soil tested was a silt loam, which is expected to be compressible. The effect of the different densities of the UFA-measured samples, which reflects the different degrees of compaction in the samples, causes shifts in the characteristic curves. While the curves measured using the UFA are reasonably reproducible, they diverge from the traditionally measured curve below 40% water content. The differences increase as the water content decreases (more compaction at higher angular velocities).

Similar results are shown in Figure 2, which shows data measured at the INEEL for the model soil (a sandy loam) used in this task and in the interfacing ESR task.⁹ The INEEL obtained the UFA-

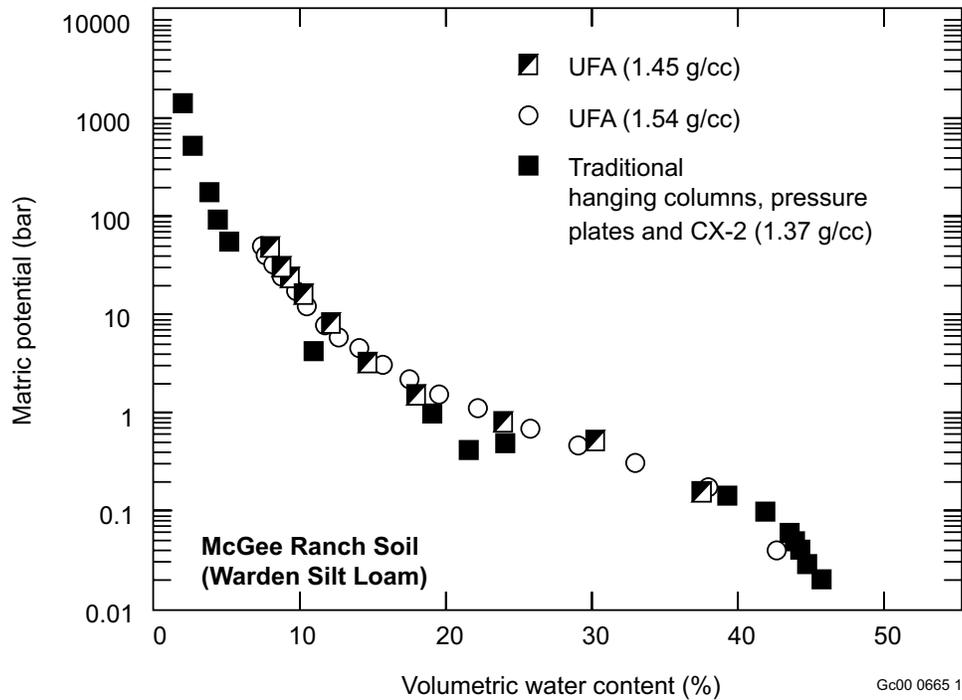


Figure 1. $\psi(\theta)$ relationships obtained using the UFA for splits of Warden Silt Loam from the McGee Ranch site in Eastern Washington State.⁷ Also shown are results on the same soil using traditional methods.⁸ (Figure adapted from UFA Ventures, 1996)

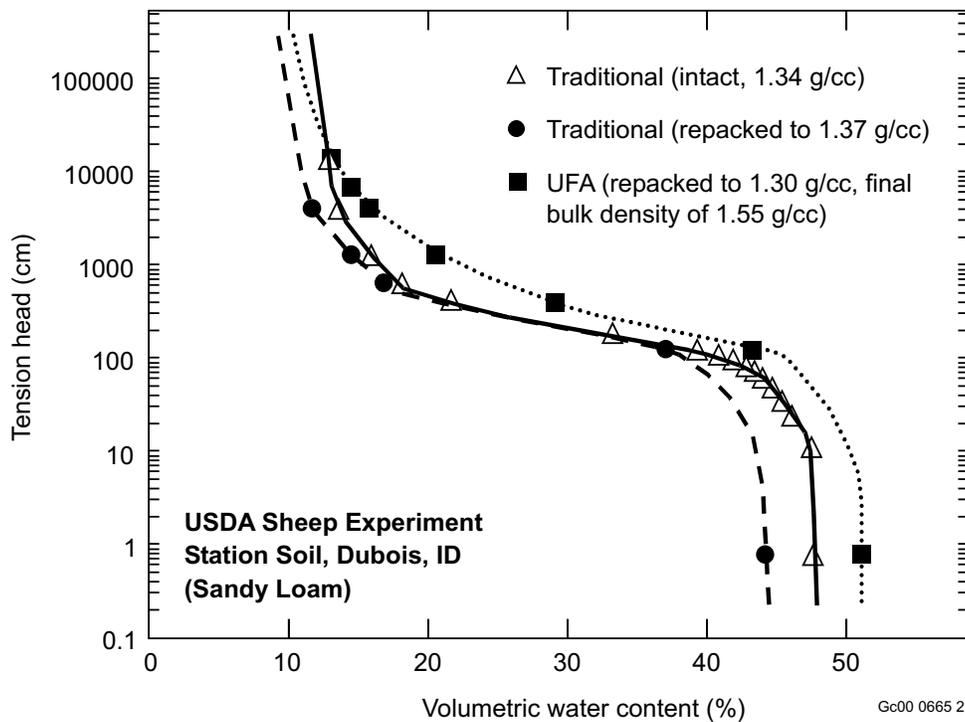


Figure 2. $\psi(\theta)$ relationships obtained using traditional methods and the UFA for splits of a sandy loam from the USDA Sheep Experiment Station in Dubois, Idaho (Reference 9).

measured data in Figure 2 through subcontract with UFA Ventures, Inc. Data are included in Figure 2 for both intact and repacked samples using the traditional methods. Note the 20% increase in bulk density for the UFA-measured sample from its initial value of 1.30 to 1.55 g/cm³. As in Figure 1, the UFA-measured curve also diverges from the traditionally measured curves below 40% water content. Our approach to these data is to determine porosity changes with increased compaction, and mathematically relate the UFA-measured curves to the traditionally measured curves. This should allow eventual relationships between UFA-compacted soil and field-compacted soil measurements.

Porosity changes can be determined using x-ray microtomography.¹⁰ X-ray microtomography measures the 3-D internal structure of a material's x-ray absorption. Hundreds of radiographs of a sample are taken at small angular increments over 180 degrees or more of sample rotation. A computer algorithm inverts these data to produce the 3-D absorption map. X-ray microtomography can resolve volume elements within a sample down to approximately 8 μ³ (2 x 2 x 2 μm), which is on the scale of the smaller interstitial pores.¹¹ It has been suggested that it is possible to create 3-D images with about 1% accuracy and a resolution of about 1 μm (see Reference 12) of real microstructures such as sandstone, coal, and biological materials. For cement mortar, a resolution of order 10 μm was sufficient to visualize the main features.¹³ At higher resolutions, other features in the mortar, such as the interfacial zone microstructure at the sand grain and or cement paste, were more apparent. Limits to the size of sample studied depended on the resolution needed. Resolution is defined as W/P, where W is the sample width and P is the number of pixels across the image width. Studying larger samples sacrifices resolution (see Reference 13).

In a recent study,¹⁴ 3-D x-ray microtomography was used to image the microstructure of two types of brick. The images were processed to remove the noise (random and circular pattern), a threshold was established to match the porosity determined experimentally, and the 3-D binary images were analyzed to estimate their vapor diffusivity and air permeability to compare to experimentally measured data.¹⁵ They concluded that care must be taken in obtaining the tomographic images at a resolution that both enables isolation and quantification of the pores of interest and provides a representative elementary volume for transport property calculations. The agreement between computed and measured properties was reasonable, suggesting that x-ray microtomography can provide valuable information on the characteristics and properties of the pore networks developed in these porous materials.¹⁴

Work Scope and Subtasks

The overall scope of this task includes a learning period for a new UFA instrument (using undeformable materials), assessments of compaction in the UFA and in hanging columns, and evaluations of how UFA and hanging column data and observations are incorporated into model parameterization. This task is separated into three subtasks:

1. Hanging Column/Pressure Cell Experiments
2. In-House Expertise with the UFA Instrumen.
3. Determining Relationships between Moisture Characteristic Curves of Compactible Soil Measured in Hanging Columns and in the UFA.

These subtasks are divided between FY 2000 and FY 2001, as follows (FY 2001 activities are shown to indicate the activities for next year):

FY 2000 Research Activities

Subtask 1. We began hanging column/pressure cell measurement of the moisture characteristic drainage curve of the compactible soil. We measured preliminary wet and dry pore size distributions of the initial soil and established collaboration with PNNL to do baseline XMT analyses of the cores.

Subtask 2. We ordered a J-6 UFA instrument from UFA Ventures, Inc., installed it at the INEEL, and completed instrument-specific training by a UFA Ventures, Inc. technician. An INEEL hydrologist spent 2 weeks in late FY 2000 in Clark Lindenmeier's laboratory at PNNL receiving direct hands-on instruction in the measurement of moisture characteristic curves and unsaturated hydraulic conductivity from experts in the use of the UFA.

FY 2001 Research Activities

Subtask 1. We will complete hanging column/pressure cell measurement of the moisture characteristic drainage curve of the compactible soil in early FY 2001.

Subtask 2. We will develop further expertise in the operation of the UFA at the INEEL while studying the effect of anisotropy on the moisture characteristic drainage curves of a sandstone and of a solid basalt.

Subtask 3. We will use the UFA to measure the moisture characteristic drainage curve of the compactible sandy loam from the interfacing ESR microbial activity task. We will use x-ray microtomography and nitrogen adsorption to estimate changes in porosity due to compaction, and develop a theoretical mathematical relationship to relate compaction and or porosity and force applied by the centrifuge.

Results for FY 2000

This task began the end of May FY 2000. Owing to the late start, most effort in FY 2000 was in procurement and installation of the J-6 UFA and in obtaining the necessary training in the maintenance and operation of the instrument. We established collaboration with Clark Lindenmeier's laboratory for a large fraction of this training, and developed methods for coring and shipping the soil to and from PNNL without disturbing the samples. Specific results are discussed below.

Subtask 1. Hanging Column/Pressure Cell Experiments

Subtask 1 work in FY 2000 consisted of developing a method for coring undisturbed, intact samples, shipping them to PNNL, scanning them by XMT, and shipping them back to the INEEL for use. Developing these methods is extremely important in obtaining reproducible hydraulic measurements from intact cores (as opposed to repacked samples) using both traditional methods and the UFA. The collaboration with PNNL to do XMT analyses offered us a rare look into the structure of the soil cores and alerted us to certain practices and materials that could cause preferential flow in the core. If preferential flow were to occur during drainage, saturated flow, or unsaturated flow, the hydraulic properties measured would not represent the true properties.

X-ray microtomography scans and analyses of our samples were measured at the x-ray Microtomography Laboratory at PNNL. Drs. Peter McGrail and Clark Lindenmeier operate the laboratory. The tomographic system is an ACTIS 200/160 KXR unit manufactured by Bio-Imaging Research. The instrument is housed in an 8,000-lb lead-lined near-zero emission enclosure and is capable of achieving a resolution in the focal plane of one one-thousandth of the object diameter. A microfocus x-ray source allows variable slice widths over a nominal range of 10 to 150 μm . Two-dimensional computed tomographic (CT) images are displayed using 256^2 , 512^2 , or $1,024^2$ pixels, each at 12 bits (4,096 contrast

levels). The instrument can also be used to obtain digital radiographs. The system comprises a Kevex model KM16010E-A x-ray tube with spot sizes of 10, 20, 65, and 250 μm at power levels of 5, 10, 50, and 160 watts, respectively. The x-ray source uses a tungsten target, and the x-rays are emitted through a 0.01-inch-thick beryllium window. The RLS-2048/100 CCD detector is a gadolinium oxysulfide scintillation phosphor screen optically coupled to a linear photodiode array through a fiber optic taper. The diode array is an EG&G Reticon RL2048S, monolithic self-scanning linear photodiode array with 2,048 photodiode sensor elements having 25- μm center-to-center spacing. A computer-controlled sample manipulator with a 75-mm-diameter turntable allows 365 degrees of continuous rotation and a maximum vertical travel of 150 mm. Larger objects (up to 150 mm) may be placed on the table using jigs. A computer data acquisition, instrument control, and image reconstruction system with ACTIS+ software provides x-ray and sample manipulation control in addition to CT and CT Multi-Planer (MPR-3D) image reconstruction. The PC is an EISA bus system running SCO UNIX.

It was necessary to choose a standard core size to eliminate the potential effects of different core diameters. We decided to subcore intact cores from sample cans containing the model soil cores (collected in October 1999 for the interfacing ESR task). Stainless steel rings, 1 in. (o.d.) \times 1.75 in. (length) with 1/32-in. wall thickness were initially used to core the samples. The soil in the cans was first saturated with water by drilling holes in the bottom of the can and placing the can into a pan of shallow water. The ends of the rings were covered with filter paper and then with aluminum plates. The plates were then clamped together (end-to-end) and shipped to PNNL for XMT analysis. The cores remained undisturbed during shipping, but we do not know whether they dried out significantly. When removed from the plates, the top and bottom few millimeters of the core were disturbed from the soil sticking to the filter paper when it was removed. Figure 3 shows an example XMT digital radiograph and an XMT cross-section at 13-mm depth. The density of the stainless steel was too high relative to the soil density to allow good resolution of the soil, seen in Figure 3 (the stainless steel is much brighter than the soil).

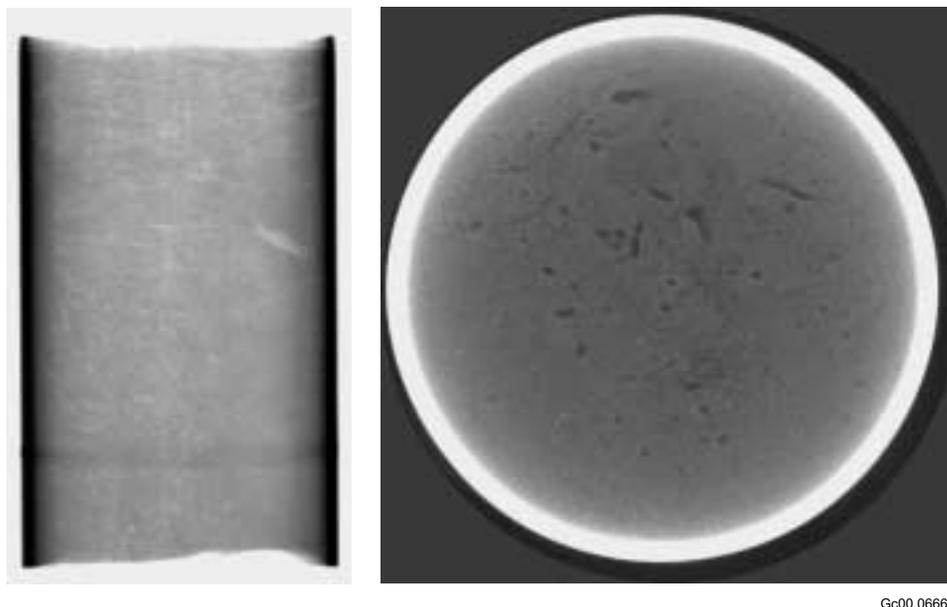


Figure 3. Digital radiograph (left) and cross-section (right) of an intact core of the model soil cored with a 1 in. (o.d.) \times 1.75 in. (l) stainless steel ring with 1/32 in. wall thickness. The concavity of the top and bottom of the radiograph are due to soil sticking to the filter paper. The density difference between the stainless steel ring and the soil was too high to allow good resolution of the soil.

To combat this effect, we used Plexiglass instead of stainless steel for the ring. The new rings were made to the same dimensions as before. Figure 4 shows a digital radiograph and cross-section at 15 mm in a Plexiglass ring, using the same shipping method. For these scans, the filter paper was left in place. Note that the lower density of the Plexiglass allowed better resolution of density differences in the soil. Also, note that the sample exhibits severe cracking around the edges of the core. While the cores seemed undisturbed at the time of shipping, they apparently were either cracked at the time of coring or they cracked while en route to PNNL. We also noted that the cores dried out completely during shipping. As shown in Figure 5, the cracks started only at the top end and decreased with depth. We hypothesize that the tension of the coring press deformed the top of the ring during coring. When the tension was released, the ring sprang back to circular and cracked the soil core within. Drying likely occurred during shipping due to an imperfect seal between the ring and the end plates. Because of this, future samples will be cored with a Plexiglass ring fitted concentrically within a stainless steel ring. After coring, the stainless steel ring will be removed, and the Plexiglass ring fitted with sealable end caps that do not apply perpendicular or axial stress to the rings.

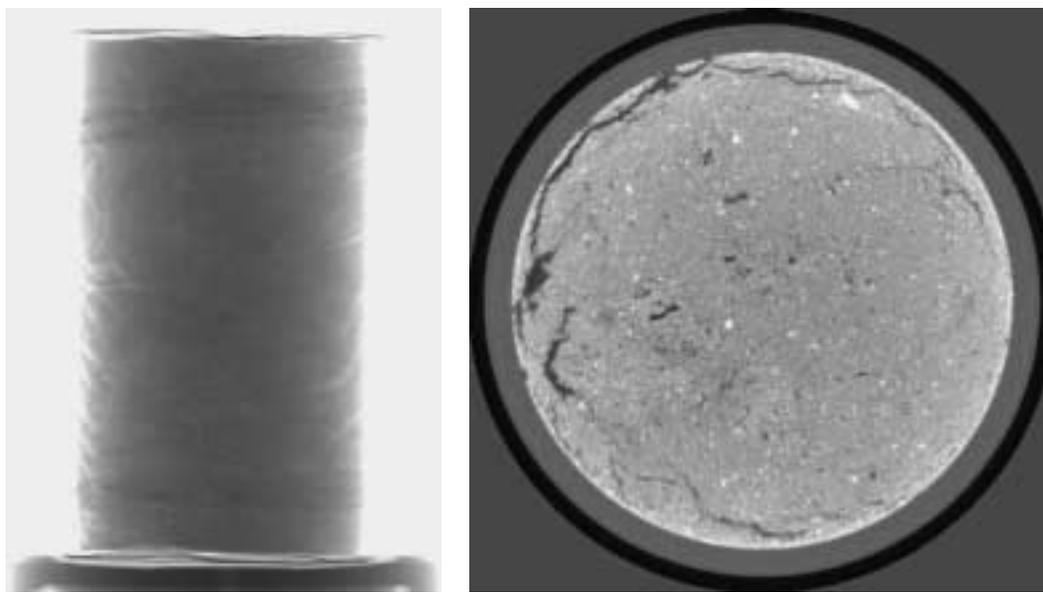


Figure 4. Digital radiograph (left) and cross-section (right) of an intact core of the model soil cored with a 1 in. (o.d.) \times 1.75 in. (l) PlexiglassTM ring with 1/32 in. wall thickness. The filter paper was left in place for these scans. The density of the PlexiglassTM was sufficient to allow good resolution of the sample.

Work on Subtask 1 will continue into FY 2001. We will test the new coring and shipping method and use the scanned cores in hanging columns/pressure cells to measure the moisture characteristic curve. These data will be compared with those shown in Figure 2 above (measured in the interfacing ESR task), and the XMT data will be used as the baseline for cores to be measured in the UFA. Obtaining reproducible results with soils is generally accomplished by homogenizing and repacking the soil in the column to the desired density. These methods lead to stratification of the soil in the column (see Figure 6), and when used in the UFA, to severe compaction (see Figure 2). Information learned thus far in Subtask 1 will prove to be invaluable in obtaining reproducible results from compactible materials in the UFA by providing a reproducible way to arrive at a consistent starting point for measurements using intact cores.

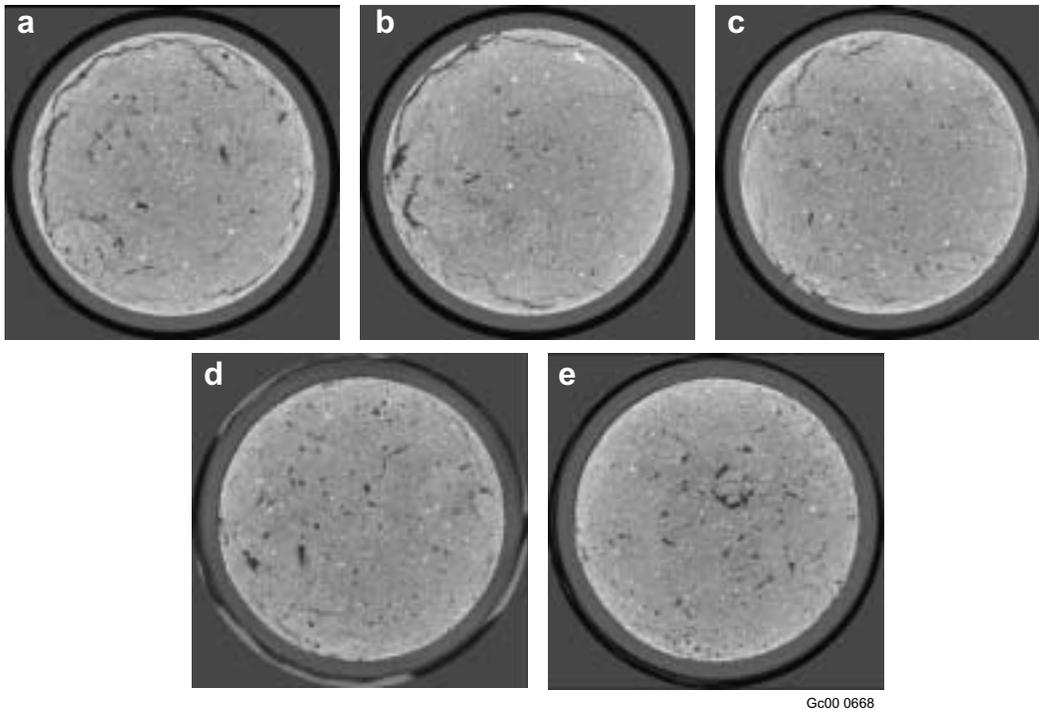


Figure 5. Cross-sections with depth of a core of the model soil. The sample was cored with a 1 in. (*o.d.*) \times 1.75 in. (*l*) Plexiglass™ ring with 1/32 in. wall thickness. Scans are (a) 8 mm; (b) 15 mm; (c) 22 mm; (d) 29 mm; and (e) 34 mm. The reduction in cracking in from only one of the ends suggests that the ring deformed at the top during coring.

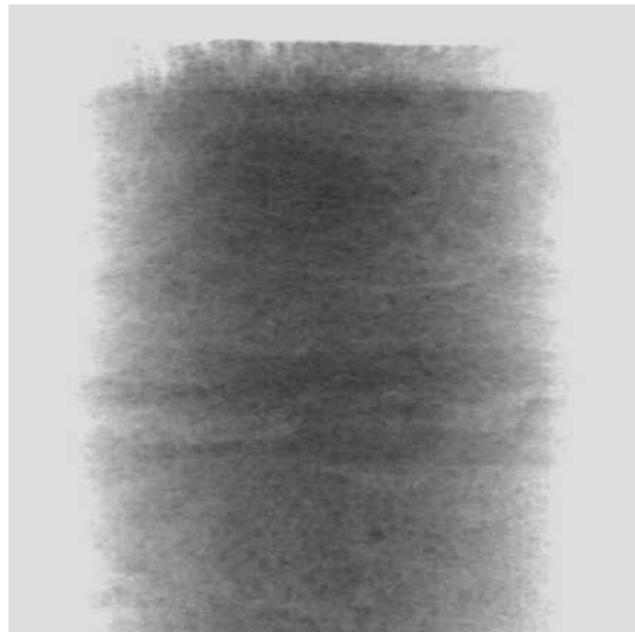


Figure 6. Digital radiograph of a repacked sample of the model soil in a J-6 UFA sample holder. The sample was repacked using standard techniques.^{16,17} Stratification is clearly seen in the sample, which would affect the moisture characteristic curve and potentially cause preferential flow.

SUBTASK 2: Development of In-House Expertise with the UFA Instrument.

Subtask 2 work in FY 2000 consisted of purchasing a J-6 UFA from UFA Ventures, Inc. (Richland, Washington) and installing it at the INEEL. Once the instrument was installed, 3 days of instrument-specific operation/maintenance training, provided at INEEL by a UFA Ventures, Inc. technician, were completed by two INEEL staff hydrologists and one lab technician. In addition, an INEEL hydrologist completed two weeks of hands-on training at PNNL in Clark Lindenmeier's laboratory. The learning period for the newly purchased J-6 UFA instrument begins in FY 2001.

ACCOMPLISHMENTS

Our accomplishment during FY 2000 are as follows:

- We established collaboration with Clark Lindenmeier at PNNL, who has significant experience in both operation and interpretation of results from UFA instruments and with x-ray microtomography (XMT)
- We devised a coring and shipping method that should allow reproducible data from replicate cores
- We purchased and installed a J-6 UFA instrument at the INEEL
- We ran preliminary XMT tests with samples cored at the INEEL and shipped to PNNL, identifying preferred methods for coring, packing, and shipping the samples to and from each site.

REFERENCES

1. UFA Ventures, Inc., "Site Characterization and Transport Measurements using the Unsaturated Flow Apparatus (UFA): Potential Cost Savings Analyses Prepared for EM-50," http://www.UFAVENTURES.COM/ufo_ventures/cost_savings.html, 2000.
2. ASTM D18.21, "Test Method For Determining Unsaturated Hydraulic Conductivity in Porous Media By Open-Flow Centrifugation," *Annual Book of ASTM Standards*, Subcommittee on Groundwater, American Society of Testing Materials, Philadelphia, Pennsylvania, 2000.
3. A. P. Gamedinger, and D. I. Kaplan, "Application of a Continuous-Flow Centrifugation Method for Solute Transport in Disturbed, Unsaturated Sediments and Illustration of Mobile-Immobile Water," *Water Resour. Res.*, Vol. 36, No. 7, 2000, pp. 1747–1755.
4. G. L. Hassler and E. Brunner, "Measurement of Capillary Pressures in Small Core Samples," *Trans. Am. Inst. Min. Metall. Eng.*, Vol. 160, 1945, pp. 114–123.
5. R. N. A. Hoffman, *Soc. Petrol. Eng. J.*, Vol. 3, 1963, pp. 227–235.
6. J. L. Conca, and J. V. Wright., *Applied Hydrogeology*, Vol. 1, 1992, pp. 5–24.
7. UFA Ventures, Inc., "Matric Potential Technical Brief," http://www.UFAVENTURES.COM/ufo_ventures/tech_briefs/matric_potential.html, 1996.

8. Fayer, M. J., M. L. Rockhold, and D. J. Holford, *Model Assessment of Protective Barriers: Part III, Status of FY 1990 Work*, Technical Report PNL-7975, Pacific Northwest Laboratory, Richland, Washington, 1992.
9. D. N. Thompson, K. E. Baker, and R. W. Smith, "Reactive Transport in Variably Saturated Heterogeneous Media: Relationships Between Moisture Content, Tension, and Biogeochemical Activity in the Vadose Zone," *Environmental Systems Research, FY-00 Annual Report*, Idaho National Engineering and Environmental Laboratory, INEEL/EXT-2000-01085, 2000.
10. J. Kinney, Q. Johnson, U. Bonse, M. Nichols, R. Saroyan, R. Nußhardt, R. Pahl, and J. Brase, *Materials Research Society Bulletin*, Vol. 13, No. 1, 1988, pp. 13–17.
11. E. Landis, D. Keane, S. Shah, E. Nagy, and D. Urbanek, "Microtomography of Cement-Based Materials," <http://www.umeciv.maine.edu/landis/XMT/Default.htm>, 1999.
12. B. P. Flannery, H. W. Deckman, W. G. Roberge, and K. L. D'Amico, *Science*, Vol. 235, 1987, p. 1439.
13. D. P. Bentz, , N. S. Martys, P. E. Stutzman, M. S. Levenson, E. J. Garboczi, J. Dunsmuir, and L. M. Schwartz, *Microstructure of Cement-Based Systems/Bonding and Interfaces in Cementitious Materials*, Vol. 370, S. Diamond et al. (eds.), Materials Research Society, Pittsburgh, Pennsylvania, 1995, pp. 77–82.
14. D. P. Bentz, D. A. Quenard, H. M. Kunzel, J. Baruchel, F. Peyrin, E. J. Garboczi, and N. S. Martys, *Materials and Structures*, Vol. 33, 2000, pp. 147–153.
15. D. A. Quenard, K. Xu, H. M. Kunzel, D. P. Bentz, and N. S. Martys, *Mater. Struct.*, Vol. 31, No. 209, 1998, pp. 317–324.
16. American Society of Testing Materials, "Test Methods for Determining Unsaturated and Saturated Hydraulic Conductivity in Porous Media by Steady-State Centrifugation," *Annual Book of ASTM Standards*, ASTM D6527-1, Philadelphia, PA, 1999.
17. Klute, A. (ed.), "Methods of Soil Analysis," Part 1, 2nd ed., *Agronomy*, No. 9, ASG, Inc. and SSSA, Inc., Madison, WI, 1986, pp. 649–650.

Environmental Computational Modeling

The objective of this Section is to develop improved computational resources at INEEL to meet current and future EM needs. To this end, computational hardware, interfaces, methods, and models must all be upgraded. Our computing infrastructure must be enhanced to support subsurface science, vadose zone roadmapping, environmental cleanup, restoration, and long-term stewardship responsibilities.

A few examples of present and future activities for which these capabilities are essential include: (a) Modeling the behavior of chemical contaminants in the subsurface; (b) Modeling of contaminated facilities before decommissioning and decontamination; (c) Producing accurate roadmaps of the vadose zone; and (d) Archiving, computing, and external interfacing.

The following task is reported in this section:

- Computing Framework for Environmental Cleanup, Restoration, and Long-Term Stewardship

Computing Framework for Environmental Cleanup, Restoration, and Long-term Stewardship

Advancing INEEL Computing in Support of the DOE-EM Mission

William R. Nelson, L. Eric Greenwade, Jerry L. Harbour, and Randall Laviolette

SUMMARY

The objective of this task is to develop a computing framework comprised of advanced computing infrastructure, improved computation models and methods, interface methods and tools, and application methods and tools to support environmental management programs at the INEEL. This computing framework is required to accelerate the development and application of scientific and engineering knowledge to address significant issues in support of subsurface science, vadose zone roadmapping, environmental cleanup, restoration, and long-term stewardship activities at the INEEL and DOE complex. There have been two major thrusts for the task, enhancing the advanced computing infrastructure for EM computing at the INEEL, and identifying the computation models and methods, interface methods and tools, and application methods and tools necessary to effectively use the computing infrastructure.

The objective of this task, in cooperation with INEEL information resource management, is to enable the INEEL to achieve a step-function increase in computing capability through implementation of two new high-speed lines and associated archival and processing equipment at the INEEL. This task has already implemented a DS-3 line (45 MB/s) to Idaho State University (ISU) and from there to the Internet2 Abilene network—Internet2 is a collaboration of educational institutions dedicated to developing and using advanced internet capabilities. Through this task the INEEL has become a Sponsored Participant in Internet2 under the sponsorship of ISU. The use of Internet2 is subject to conditions focused on university research collaborations; our primary use of the Internet2 connection will be to stimulate collaboration among INEEL and INRA universities on research programs addressing DOE environmental management programs.

In cooperation with INEEL Information Resource Management this ESRC task will coordinate the installation of a new 155 MB/s OC-3 line to DOE's energy sciences network ESnet, through which INEEL researchers will be able to access high-end computing resources at other DOE national laboratories and elsewhere. Also, this ESRC task will invest approximately \$2.4M in processing and archival hardware to allow full use of the enhanced external connectivity. This will include a shared memory processor (SMP) capable of handling approximately 64 to 72 processors, and approximately 70 terabytes of onsite data storage. These capabilities will allow INEEL researchers to perform complex calculations and simulations at other computing facilities, transfer the resulting data files to the INEEL, and store, manipulate, and visualize the data here at the INEEL. In conjunction with the new high-speed data connections, this will allow INEEL researchers to collaborate with other environmental management researchers at other DOE facilities, universities, and federal agencies.

These task activities are leading to significant improvements of the EM-focused computing infrastructure at the INEEL. Installation of the planned OC-3 line will increase the maximum data transfer rate into and out of the INEEL by a factor of 100 times. The installation of the new archival and processing equipment will improve the maximum processing rate by a factor of approximately 10 times. The development of the overall architecture and framework will increase the effectiveness of the use of EM computing capabilities at the INEEL. Taken together, the improvements initiated in FY 2000 lay the

foundation to enable the INEEL to apply advanced computing technologies to the solution of the major scientific and technical issues facing EM programs.

During FY 2001 we will focus on procuring and installing archival and processing equipment, integrating the new equipment with the OC-3 line following its installation, and developing prototype modeling, analysis, and visualization tools to demonstrate the effectiveness of the EM computing framework.

The task was initiated on June 1, 2000. In the period from June 1 to September 30, 2000, we accomplished the following:

- We interviewed environmental management project personnel and computational modelers to identify computing needs
- We developed the infrastructure procurement strategy for archival and processing equipment for EM computing
- We installed the DS-3 line (45 MB/s) from the INEEL to ISU
- We obtained Secondary Participant membership in the University Consortium for Advanced Internet Development (Internet2)
- We coordinated investment of INEEL internal funds to install an OC3 line (155 MB/s) from the INEEL to the DOE Energy Sciences Network (ESnet) at Lawrence Livermore National Laboratory.

TASK DESCRIPTION

Many environmental challenges would benefit from more effective use of scientific computing and simulation capabilities. This task focuses on developing a computing framework at the INEEL to support subsurface science, vadose zone roadmapping, environmental cleanup and restoration, and long-term stewardship. The resulting computing framework will be comprised of the computing infrastructure, computation models and methods, interface methods and tools, and applications methods and tools that will be integrated to address the EM needs identified above. Figure 1 shows the conceptual structure of the EM computing framework being developed by this task. The computing infrastructure will consist of high speed links to offsite computing resources and research programs at other DOE facilities and universities, a data archival system to provide local storage for large calculations performed offsite, and onsite processing systems to enable INEEL users to extract information from the stored data for local analysis. A phased approach is being used to ensure that the infrastructure and research products produced by this program satisfy the requirements of environmental management programs at the INEEL each step of the way. An integrated approach combining links to other DOE facilities with onsite storage and processing systems is the cost-effective way to meet EM computing needs at the INEEL.

As shown in Figure 1, the EM computing framework will enable INEEL researchers to address the major categories of environmental management issues. For example, in the category of above-ground issues, (a) advanced simulation and modeling of a facility to be decommissioned will allow further cost reduction, waste volume reduction, and radiation exposure reduction as decontamination and decommissioning (D&D) engineers explore options and “what-if” scenarios; (b) operations personnel can simulate actual D&D operations; and (c) stakeholders can examine the ramifications of different choices. Advanced D&D options are being explored in other tasks described in this report, for example,

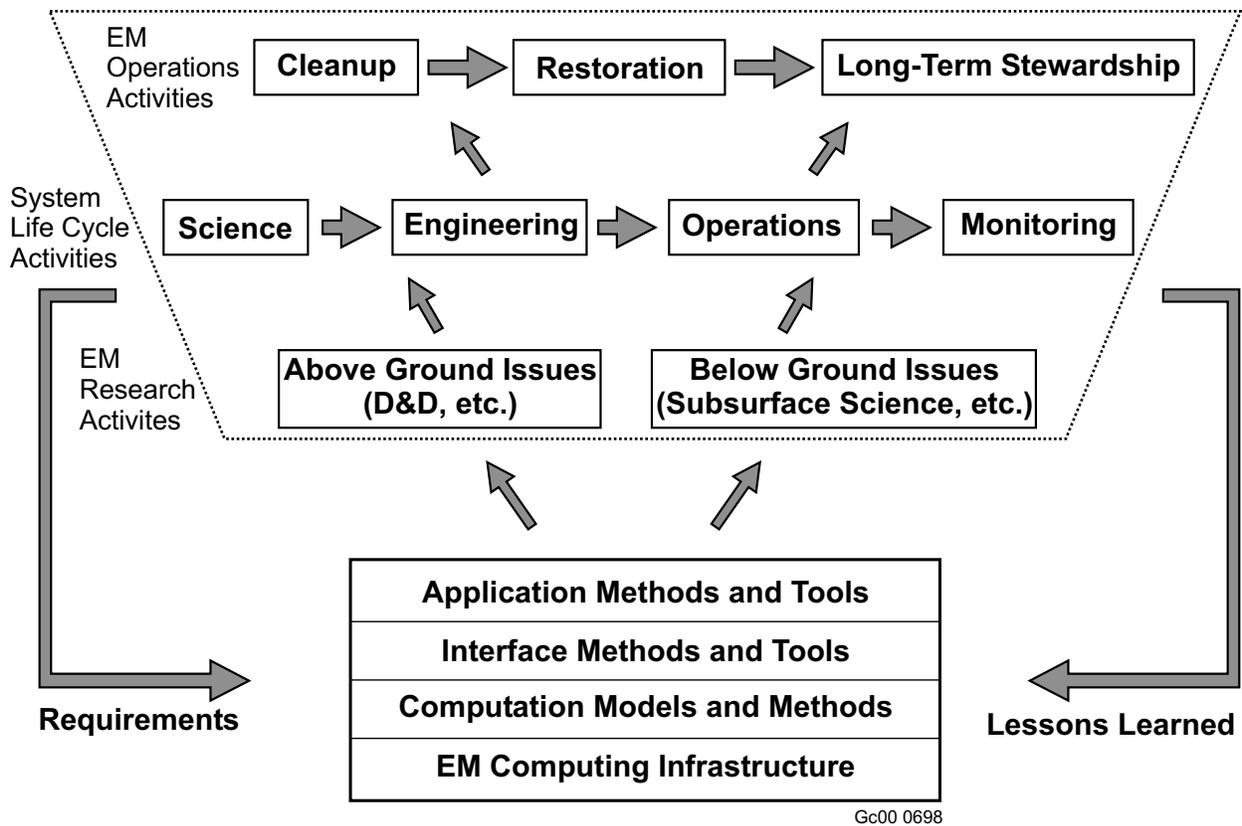


Figure 1. Illustration of conceptual structure of the EM computing framework being developed by this task.

Automated Planning for D&D of Contaminated DOE Facilities, Automated Waste Characterization for D&D of Contaminated DOE Facilities, and Automated Waste Packaging for D&D of Contaminated DOE Facilities.

In the category of subsurface issues, the computing infrastructure and framework will assist the development of sophisticated modeling techniques and algorithms to allow the simulation of complex subsurface phenomena. Advanced subsurface methods are being explored in other tasks described in the ESRC report, especially report B040, “Complex Systems Theory Applied to Subsurface Transport.”

This task is working to enable the simulation of a variety of complex phenomena in ways that are more meaningful to researchers, decision-makers, and technology developers. The goals of INEEL activities are to identify the computing and simulation needs for resolution of major environmental problems, develop the required capabilities, and develop and evaluate methods that allow effective application of scientific knowledge to the design and operation of environmental cleanup technologies. This task is specifically seeking to identify and evaluate sophisticated modeling techniques and algorithms to allow the simulation of complex subsurface phenomena. Also, this work examines the use of advanced human-machine interfaces and analytic tools to more effectively use the results of environmental simulations to support decision making. Finally, a major emphasis is to develop computing capability and infrastructure at the INEEL with an emphasis on current and potential future applications to EM programs.

ACCOMPLISHMENTS

Computing Infrastructure Development

Based on systematic analysis of the issues facing INEEL environmental management computing, the following key issues were identified, through interviews with key subsurface geoscience modelers and EM project personnel at the INEEL, that need to be addressed in upgrading the INEEL computing infrastructure:

- Current computer analyses for full-scale field problems of 10,000 to 15,000 nodes take anywhere from 4 days to months using existing INEEL computing capabilities.
- Such analyses effectively tie up available onsite computing resources and prevent their use by other projects and programs.
- Future subsurface science modeling efforts will require greater nodalization (e.g., 10^6 to 10^8 nodes to explore transport phenomena in greater detail over larger areas).
- Long-term stewardship models require calculations for periods up to 10,000 years.
- There is a need to run coupled (physical/chemical/biological) models.
- There is a need for visualization of large data sets.
- There is a need to run 4-D (space and time) D&D models to allow exploration of “what-if” scenarios to consider how best to D&D a facility.
- There is a need for collaboration with other environmental management research programs at other DOE laboratories and universities.
- There is a need to transfer large data files (e.g., 10^{11} to 10^{13} data points) from offsite computing resources to the INEEL in a reasonable time.
- The planned Subsurface Geosciences Laboratory (SGL) will include high-end visualization and virtual environments requiring the processing and transfer of large data sets.
- There is a need to perform teleconferencing, file transfer, group analyses, and virtual collaboration for subsurface science and long-term stewardship programs.

Recognizing that it will require a long-term strategy to upgrade and maintain environmental management computing capabilities at the INEEL, we developed a balanced acquisition strategy so that funding resources available for this task could provide an initial platform upon which future investments could be added to ensure that computing resources keep pace with programmatic needs. The plan developed for this task includes acquisition of high-speed offsite connectivity, onsite data archival, and onsite processing capacity.

A dual approach has been developed to provide near-term and longer-term connectivity to offsite computing resources as the INEEL's needs grow. The first step implemented a DS-3 (45 MB/s) connection to ISU in Pocatello, 50 miles south of Idaho Falls. This connection allows the INEEL to use another DS-3 connection from ISU to the University of Utah (Salt Lake City, UT, 200 miles south of

Idaho Falls) and Internet2. This connection was installed and tested during September 2000. At the same time, the INEEL was approved for Internet2 Secondary Participant status under the sponsorship of ISU.

An agreement was reached with the INEEL Information Resources Management organization to implement a (OC-3) connection (155 MB/s) to the ESnet at Lawrence Livermore National Laboratory. When this connection is installed during FY 2001 we will have increased our maximum data transfer rate by a factor of 100 compared to the situation prior to this task. In addition, we will have direct access for collaboration with other DOE laboratories through ESnet and university researchers through Internet2. This dual pathway architecture will maximize INEEL's opportunities to conduct collaborative environmental management research.

We have developed the strategy for procurement of archival and processing capabilities, and expect the equipment to be installed early in FY 2001. The majority of the investment will be used to procure a large memory shared memory processor. The current target is for a machine of at least 64 next-generation processors with a minimum of 64 GB of main system memory.

There will also be a substantial investment in data archival and storage capabilities including a 5.3 TB high performance disk array and a 65 TB tape archival system, all managed by a Hierarchical Storage Management (HSM) system that allows the entire data system (~70 TB) to act as an integrated data management environment. The HSM software allows the disk system to act as a 'window' onto the much larger tape library, automatically shuffling data between the two media types, hard disk and tape, on an as-needed basis. This equipment will be used to store both simulation and experimental results. Included in this will be those produced at the INEEL and those produced offsite and transferred to the INEEL via the new high-speed communication links.

The procurement strategy has been finalized and approved. Delivery and installation of the archival and processing equipment will occur early in FY 2001.

Computing Framework Application Development

Nine interviews were conducted to gain a better understanding of subsurface-related process tasks and associated computer application and graphical user interface needs. Eight of those interviews were held with scientists representing diverse disciplines, and the ninth was held to gain a senior management perspective. The interviews revealed that a very "basic" scientific inquiry process underlies most subsurface-related endeavors. In its simplest form, the process involves four major task elements: data collection and or acquisition, data processing, data Interpretation, and communication of interpreted results.

Despite the diversity of individuals interviewed, a surprising consensus was expressed concerning specific computer application needs. Frequently these needs were expressed under the topics of real-time linkages, remote access, in situ and telemonitoring capabilities, data archiving and retrieval, visualization, computation, information manipulation and configuration, data management, hypertext linkages via the Internet, Geographical Information Systems , 3- and 4-D modeling, simulation, and remote access to mobile laboratories. These various concepts have been grouped under the following four broad application need areas:

- *Remote access to field and laboratory experimental sites* from office work stations or other distal settings. Remote access was frequently expressed in terms of remotely accessing collected data. However, it was also expressed in terms of being able to establish some type of visual linkage, indicating the need to create a type of visual "telepresence" in a virtual environment. This whole generic application area is perhaps best identified as telescience—

an emerging area using technological advancements (specifically telecommunications and informatics' technologies or "telematics") to remotely conduct scientific research.

- *A subsurface information management system (SIMS)* that would represent the SGL's data repository and communal relational database. Such a system could ideally do everything from tracking field and laboratory samples to archiving raw geophysical data. As such, the proposed system would have to serve as a repository for a wide array of data types, including alphanumeric, 2-D and 3-D graphical, video, and still photos.
- *2-D, 3-D, and 4-D (temporal) visualization capabilities* that support both independent and group visual exploration of large data sets. An important need may be to create dedicated collaborative "visualization rooms" that allow small work teams to interactively view, explore, interpret, manipulate, configure, analyze, and discuss large data sets for extended periods. Such visualization "experiences" must enhance group facilitation and communication, as well as data exploration and understanding. As such, it is important to create a viewing experience that does not impede communication between and among team members.
- *A communications network* that permits widespread group collaboration and data exchange among diverse individuals and remote site locations. Easily accessible and executable two-way communication and data exchange must be developed if the concept of conducting "research campaigns" involving diverse disciplines and physically separated personnel is to be successful.

In summary, the activities performed in FY 2000 for the "Computing Framework for Environmental Cleanup, Restoration, and Long-term Stewardship" task have developed a strong foundation for providing the computational resources and capabilities to accomplish the goals of a wide variety of Environmental Management programs at the INEEL and throughout the DOE complex.

REFERENCES

None

Environmental Systems Science and Technology

This area of research explores novel processes or materials to treat, decontaminate, and store hazardous and radioactive waste, which includes several tasks that will assist decommissioning activities.

The following tasks are reported in this section:

- Decontamination, Decommissioning, and Remediation of Optimal Planning System for the Advanced Decontamination and Decommissioning System
- Waste Characterization and Sorting Station for the Advanced Decontamination and Decommissioning System
- Robotic Waste Packaging System for the Advanced Decontamination and Decommissioning System
- Environmental Separations and Barriers
- Proton Conducting Ceramic Membrane Applied to Spent Nuclear Fuel Stewardship
- Spectroscopic Investigations at Solid Supercritical Fluid Interfaces in Support of Advanced Supercritical Separation Techniques

Decontamination, Decommissioning, and Remediation Optimal Planning System for the Advanced Decontamination and Decommissioning System

Automated Planning for Decontamination and Decommissioning of
Contaminated DOE Facilities

Julia L. Tripp, Michael G. McKellar, and Mark Landon

SUMMARY

The current baseline decommissioning techniques being used are labor intensive and extremely costly. Decontamination and decommissioning (D&D) liability-holders require new and improved technologies that significantly reduce costs and improve safety. The Decontamination, Decommissioning, and Remediation Optimal Planning System (DDROPS) is a computer-based planning system previously developed at the INEEL that allows an operator to model a facility for remediation preplanning and waste minimization purposes. DDROPS incorporates solid geometric modeling and optimization techniques to help identify locations for segmenting contaminated materials (pipes, tanks, etc.) to improve packaging densities within waste boxes, and minimize radiation exposure to D&D workers.

The work to be completed as part of this task includes (a) completion of optimal tank cutting and incorporation of the effect of different cutting tools, (b) completion of radiation exposure calculations and visualization of exposure to individuals performing work tasks on the 3-D model, (c) completion of the 3-D model of the contaminated facility, and (d) integration of various portions of DDROPS (radiation visualization, optimization, 3-D modeling, radiation calculations, etc.) into one coherent package. All of these tasks were started in FY 2000 and will be completed in FY 2001.

The potential benefits from this task will be a reduced personnel radiation exposure and a minimized number of waste containers required for a given volume of waste.

TASK DESCRIPTION

Background

The DDROPS developed by the INEEL is a computer-based planning system in which an operator can simulate a facility for remediation preplanning and waste minimization purposes. To improve packaging densities within waste boxes, DDROPS incorporates solid geometric modeling via Parametric Inc.'s Pro/Engineer software and proprietary algorithm/optimization techniques to help identify locations for segmenting contaminated materials (pipes, tanks, etc.). It also includes visualization of radiation fields and the capability to calculate the radiation dose to an individual working or walking through the model, and can thus be used to minimize radiation exposure to D&D workers. The system includes smart databases, proprietary code/algorithms, geometry model preprocessors, and robotic path planners.

DDROPS is valuable for operator training, operation planning, and historic preservation. Through the use of DDROPS, an operator first creates a simulated model of the facility to be dismantled. The operator can then move throughout the model to familiarize themselves with the surroundings without becoming exposed to the hazards of the actual facility. By accessing a series of proprietary code/algorithms an operator can preplan the entire D&D operation.

D&D operations involve a considerable amount of equipment removal and object segmentation. Through DDROPS, an operator can determine the optimal location for making all required object cuts and facility dismantlements. This optimization is calculated as a result of operator-controlled constraints, such as waste dimensions, radiation levels, mass properties, schedule, etc. Following the virtual segmentation, an operator can continue to model the operation through the packaging stage until all segmented objects are placed into the various waste containers. A manifest/object inventory generation procedure is also maintained to provide the operator with a complete record of waste packages.

A number of the nuclear facilities now undergoing D&D are one-of-a-kind, state-of-the-art facilities. Some of these facilities are being remediated for additional use while others are being completely dismantled. In either case, a detailed record of their condition is required. DDROPS provides a means of capturing and maintaining an improved historic and visual record of the facility. This record is vital to updating as-built drawings as well as providing a complete record of dismantled facilities.

The INEEL has implemented DDROPS during D&D operations at the INEEL's Central Facility Area (CFA) Sewage Treatment Plant (CFA-691) (Figure 1) through the EM-50 funded Accelerated Site Technology Deployment Idaho D&D Project. The facility demolition, completed according to normal practices, resulted in six waste boxes. The DDROPS estimate, using optimal cutting, was two boxes. The results of this implementation have shown the system provides several significant benefits. For example, the use of DDROPS results in waste containers with a greater packaging density as compared to conventional techniques. This in turn reduces the volume of waste—three times less in this implementation—transported for disposal, resulting in a direct decrease in D&D disposal costs. Second, a reduction in worker exposure can be realized by familiarizing workers with the hazardous environments without exposing them to actual hazards.

A patent (No. 5936863) was awarded on this Optimal Segmentation and Packaging Process. A paper titled "Optimal Planning of Decontamination, Decommissioning and Remediation" was presented at the ANS 8th International Topical on Robotics and Remote Systems and one titled "Technology Demonstration and Deployments at the INEEL" was presented at WM-99 (See Appendix A).

Subtasks

The DDROPS modifications to be completed as part of this task include optimal cutting of nonpipe parts, incorporation of radiation visualization and calculation of worker exposure into the models, and integration of DDROPS into a coherent software package. The subtasks for this task include:

- Completion of optimal tank cutting and incorporation of the effect of different cutting tools
- Completion of radiation exposure calculations, visualization on the 3-D model, and calculation of worker exposure
- Completion of a 3-D model on a contaminated facility
- Integration of the various portions of DDROPS into one coherent package.



Figure 1. A DDROPS model of a facility undergoing D&D.

The optimal tank cutting procedure was completed in FY 2000 (see Figure 2). Radiation exposure calculations were started on a Test Area North facility, TAN-616 (a liquid waste treatment facility shut down in 1970), and a new 3-D model of the facility was started in FY 2000. The characterization of TAN-616 for decommissioning is currently being completed. Existing data shows that some areas of this facility, in particular the evaporator pit, have very limited access and fairly high radiation levels, which adds credence to performing detailed planning to better protect worker health and safety. Investigation into the best approach to integrate the various portions of DDROPS into one coherent package was also completed.

Need for DDROPS

Although industry can successfully perform D&D operations by using a variety of baseline techniques, these techniques are labor intensive, extremely costly, and result in considerable volumes of waste. It is expected that the amount of radioactive waste to be generated during decontamination, decommissioning, and remediation of DOE's nuclear and associated facilities is significant. This waste, and its subsequent disposal, will have a direct impact on the operational costs associated with the D&D operations of these facilities. As such, the cost of remediating these facilities with baseline technologies

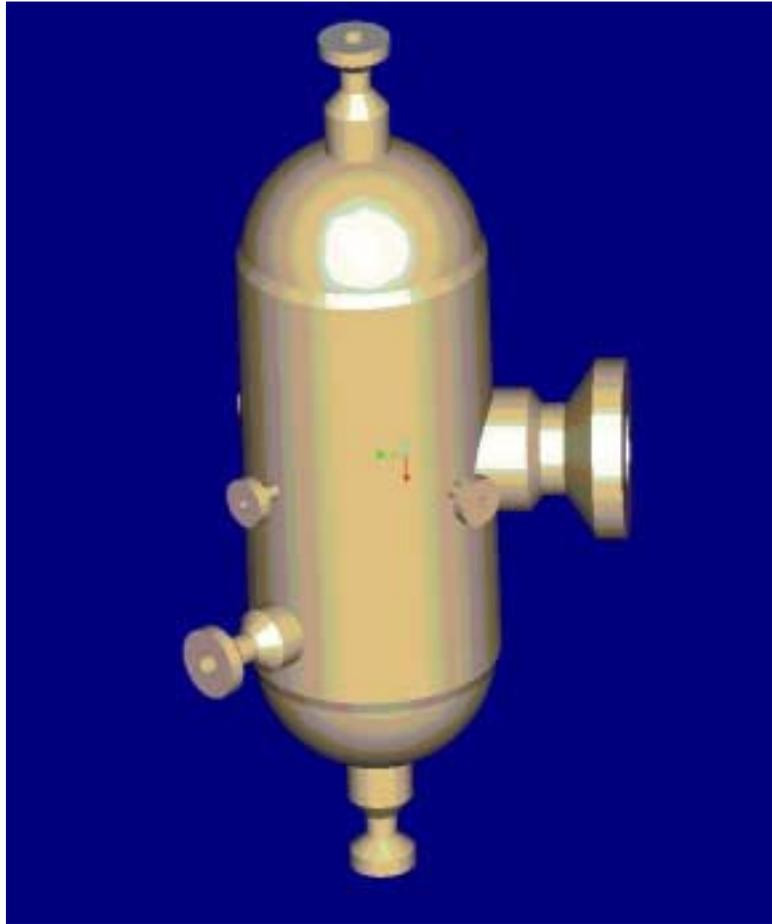


Figure 2. DDROPS algorithms used to optimally cut simulated tanks for disposal.

has been estimated to be in excess of \$36 billion. For this reason, DOE and other commercial D&D liability-holders require new and improved technologies that provide significant cost and safety improvements over conventional technologies.

The INEEL recognizes the need to advance technical solutions that can significantly reduce the cost of performing D&D operations, and has taken an aggressive role in integrating its D&D operations with its applied engineering expertise. This integration allows INEEL facilities to be used as test beds for evaluating, demonstrating, and deploying innovative D&D technologies that generate less secondary waste, cost less, require less labor, reduce exposure of personnel to radioactive and hazardous materials, and improve safety for workers and the environment.

This task deals specifically with several needs identified by the Idaho Site Technology Coordination Group (STCG), including removal of two reactors as single units, remote demolition of machinery, remote demolition of metal structures, and remote demolition of piping.

It also offers opportunities for lowering the need for long-term monitoring by allowing more cost-effective cleanup and removal of contaminated sites, thus reducing the number of facilities requiring long-term stewardship. Possible applications to EM problems beyond this work package and funding, such as planning for D&D of subsurface burial sites and waste management, will be researched.

R&D/Operations Integration

The INEEL Facilities Deactivation Department conducts D&D activities at the INEEL. Representatives from this group have been involved in reviewing this technology and giving ideas on needed improvements. They have already implemented portions of DDROPS to obtain planning information to aid in safe removal of an underwater reactor (see Figure 3) and estimate waste packaging, as previously mentioned. D&D operations personnel have continued to express an interest in using the system, and a willingness to demonstrate it, once it is completed.

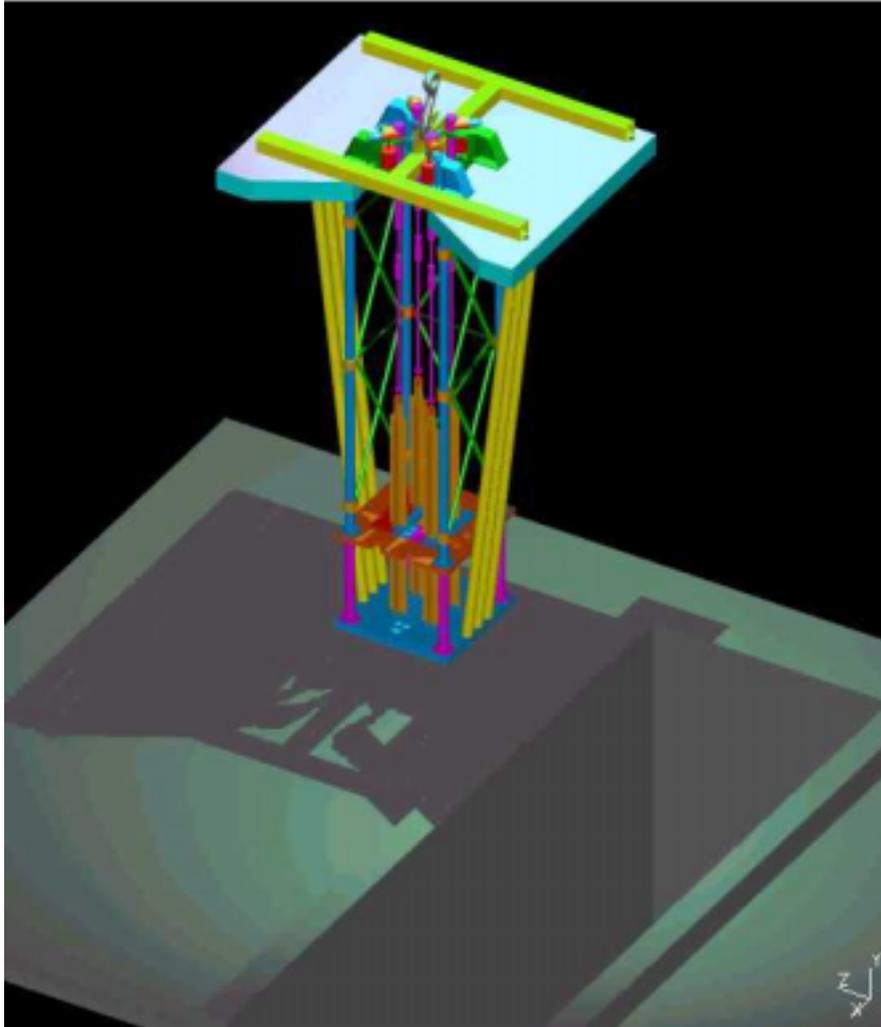


Figure 3. Reactor simulation done with DDROPS.

Requests for information and possible deployment have been received from the Savannah River Site, Mound, and Rocky Flats. Presentations on this technology have also generated much interest in the commercial area.

Possible Future Activities

The following bullets describe some of the future activities being pursued:

- Discussions have been held with Human Factors personnel on possible related technologies which could be used to refine the DDROPS system using avatars.
- Ongoing discussions are being held with the Atomic Energy Authority of the United Kingdom, London (AEA) to determine the applicability of DDROPS to their D&D operations. An umbrella work for others contract is already in place.
- DDROPS was a technology included in a contractor's bid for an SRS project.
- DDROPS is a technology included in a proposal for the EM-50 funded Large Scale Demonstration and Deployment projects. The award of these proposals will be announced in December 2000.
- Ongoing discussions are being held at Rancho Seco with the Electric Power Research Institute to deploy new D&D technologies, such as DDROPS. An unsolicited proposal was submitted to the National Energy Technology Laboratory in October 2000.

ACCOMPLISHMENTS

Our FY 2000 accomplishments are as follows:

- The optimal tank-cutting task is completed and the incorporation of different cutting tools has started.
- A decision was made to model the evaporator pit at the TAN-616 facility, which is slated for D&D soon. In addition, a demonstration of some new technologies is being planned at this facility. The blueprints of the facility were pulled and the modeling effort was started.
- An initial overview of the requirements of software integration were completed. The integration will take place in FY 2001 as the various pieces of this program become available.

REFERENCES

None

Waste Characterization and Sorting Station for the Advanced Decontamination and Decommissioning Systems

Automated Waste Characterization for Decontamination and Decommissioning of Contaminated DOE Facilities

Julia L. Tripp and Douglas W. Akers

SUMMARY

Current baseline decommissioning techniques are labor intensive and extremely costly. Decontamination and decommissioning (D&D) liability-holders require new and improved technologies that will significantly reduce costs and improve safety. One of these new technologies is the Waste Characterization and Sorting System (WCSS). Once completed, the WCSS will support material identification and characterization, sorting and recycling during the disassembly process, and accurate manifestation of waste containers. WCSS will determine physical measurements, including weight, volume, and density, isotopic radiological characteristics, and metal composition of each waste item. This information can then be sent to a central database. The system will be designed to require limited operator interaction as it will have a number of self-test functions, including calibration, that will notify the operator if the system is not operating correctly or if the item being processed is outside the waste characteristics appropriate for characterization or disposal.

The work for this task is separated in four subtasks: (a) building the scanning/conveyor system, (b) completing the graphical user interface and software modifications required to run the system as an integrated unit, (c) completing the gamma spectrometry algorithms and calibration system, and (d) completing integrated system testing. The scanning/conveyor system assembly was completed in FY 2000, all other subtasks were started in FY 2000 and will be completed in FY 2001.

The WCSS system will provide the unique capability and algorithms to determine detector efficiencies for each waste item as it is processed and perform quantitative gamma-ray spectrometry on D&D waste without a trained operator. This capability will allow the system to be replicated and used to produce systematic and reproducible quantitative analysis results for wastes from numerous sites. This has a number of benefits to help meet proposed DOE and Nuclear Regulatory Commission (NRC) regulations concerning the "free-release" of scrap metal and other wastes for reprocessing and disposal at locations other than low-level radioactive waste disposal sites. Other potential benefits from this task will be improved waste characterization through automation, reduced personnel hazards exposure, and a more accurate manifestation of waste containers.

TASK DESCRIPTION

Background

A basic waste characterization system was previously developed as part of the ROVER decommissioning project. This ROVER system will be used as the basic platform for the WCSS. The ROVER Waste Assay System (RWAS) is a nondestructive assay system designed for the rapid assay of U^{235} contaminated items. A scanning system translates a NaI(Tl) detector/collimator system over the structural components where both relative and calibrated measurements for Cs^{137} are made. U^{235}

concentrations are determined from $C^{137}:U^{235}$ ratios measured by radiochemical methods. The system, currently in operation, is sufficiently automated that the computer system does the system calibration, problem identification, collimator control, data analysis, and reporting. However, to make it more applicable for D&D field work, it needs to be upgraded to increase its automation and efficiency.

Subtasks

The following upgrades need to be added to the WCSS:

- An automated component recognition system to the basic system to define the item volume and shape based on a laser scanning technique
- An automated calibration technique that uses the volume and weight data (density) to determine the quantities of radioactive or hazardous materials associated with a particular component
- A computerized self-testing system that allows the characterization system to determine whether it is working correctly
- A camera system with digital interface for data storage
- A conveyor system
- Other capabilities, such as automated waste sorting, automated weighing, and a germanium gamma ray detector with appropriate detector efficiencies for standard waste types expected at D&D waste sites.

Need for WCSS

Although industry can successfully perform D&D operations by using a variety of baseline techniques, these techniques are labor intensive, extremely costly, and result in considerable volumes of waste. The amount of radioactive waste expected to be generated during the decontamination, decommissioning, and remediation of DOE's nuclear and associated facilities is significant. This waste, and its subsequent disposal, will have a direct impact on the operational costs associated with the D&D operations of these facilities. As such, the cost of remediating these facilities with baseline technologies has been estimated to be in excess of \$36 billion. The DOE and other commercial D&D liability-holders require new and improved technologies that will significantly reduce cost and improve safety over conventional technologies.

The INEEL has recognized the need to advance technical solutions that can significantly reduce the cost of performing D&D operations and has taken an aggressive role in integrating its D&D operations with its applied engineering expertise. This integration allows INEEL facilities to be used as test beds for evaluating, demonstrating, and deploying innovative D&D technologies that generate less secondary waste, cost less, require less labor, reduce exposure of personnel to radioactive and hazardous materials, and improve safety for workers and the environment.

This task also offers opportunities to decrease the need for long-term monitoring by allowing more cost-effective cleanup and removal of contaminated sites, thus reducing the number of facilities requiring long-term stewardship.

Possible Future Activities

Future activities being pursued include:

- Ongoing discussions are being held with the Electric Power Research Institute (EPRI) to deploy new D&D technologies, such as WCSS, at Rancho Seco. An unsolicited proposal was prepared and submitted to the National Energy Technology Laboratory in October 2000.
- An outside commercial vendor, Perkin Elmer, has expressed continuing interest in the WCSS. This interaction is being addressed through the INEEL Technical Transfer Department.
- Both the NRC and DOE have been interested in the completed system as it provides an implementing technology that can be licensed for characterization of wastes for disposal without operator induced uncertainties.

ACCOMPLISHMENTS

The hardware assembly subtask for the WCSS was completed using parts from a similar old system, parts purchased last fiscal year, and parts ordered this year. It has been mounted in a box on the scanning bed and is integrated into one cable from the various instruments (see Figures 1 and 2).

Initial system testing is being completed to establish software requirements, and the laser curtain/conveyor belt software is functioning.



Figure 1. View of assembled WCSS hardware.

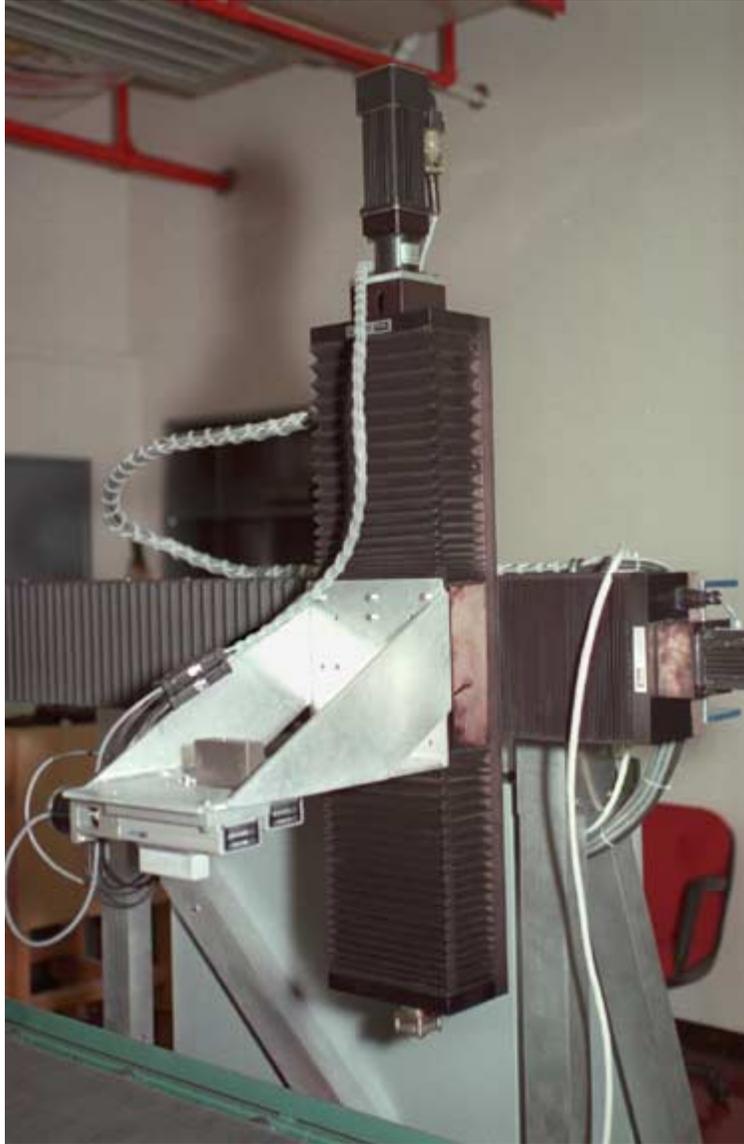


Figure 2. Closer view of the assembled WCSS collimator.

REFERENCES

None

Robotic Waste Packaging System for the Advanced Decontamination and Decommissioning Systems

Automated Waste Packaging for Decontamination and Decommissioning of Contaminated DOE Facilities

Julia L. Tripp and Cal D. Christensen

SUMMARY

The DOE weapons complex has been transitioning from a production to an environmental restoration mode. The result is costly decommissioning of a large number of facilities. The nuclear utility industry, organizations responsible for university reactors, nuclear laboratories, research reactors, and other laboratory test facilities, all face similar challenges. Unfortunately, the present baseline decommissioning techniques are inadequate. Decontamination and decommissioning (D&D) liability-holders require new technologies that provide less labor, cost savings, and safety improvements.

This task focuses on the development of a Robotic Waste Packing System (RWPS) that will perform the material handling, optimal waste packaging, and sorting/recycling step of the D&D process. A RWPS material sorting station will be designed and a prototype constructed. This material sorting station will receive waste materials, geometrically identify each piece using a state-of-the-art vision system, physically move the piece to a waste container, orient it, and place it inside (Figures 1 and 2). The RWPS material sorting station will be designed to work in conjunction with the Waste Characterization and Sorting System and to fit into the envelope of a mobile trailer. This task will also include research into real-time optimal packaging of the waste. All of the tasks were started in FY 2000 and will be completed in FY 2001.

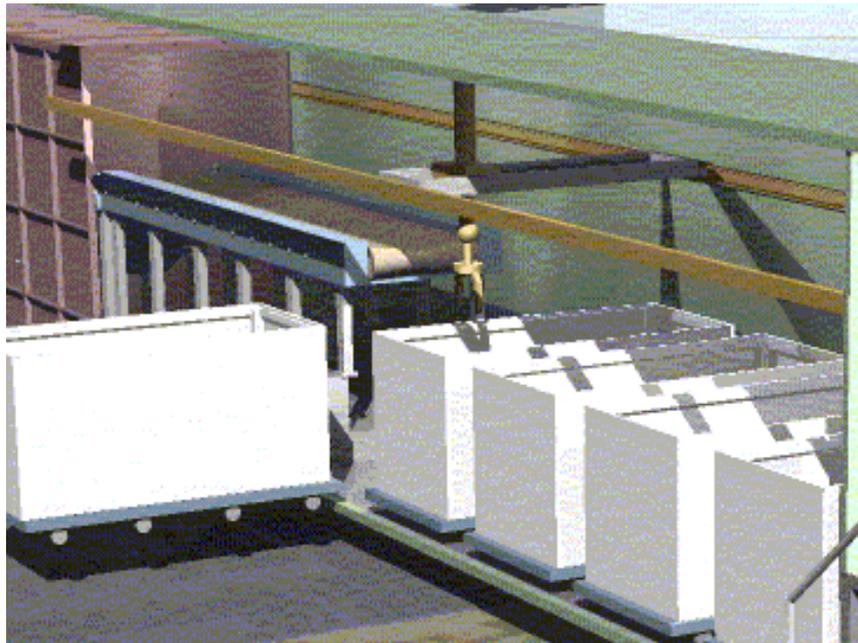


Figure 1. Conceptual robotic waste packaging system.

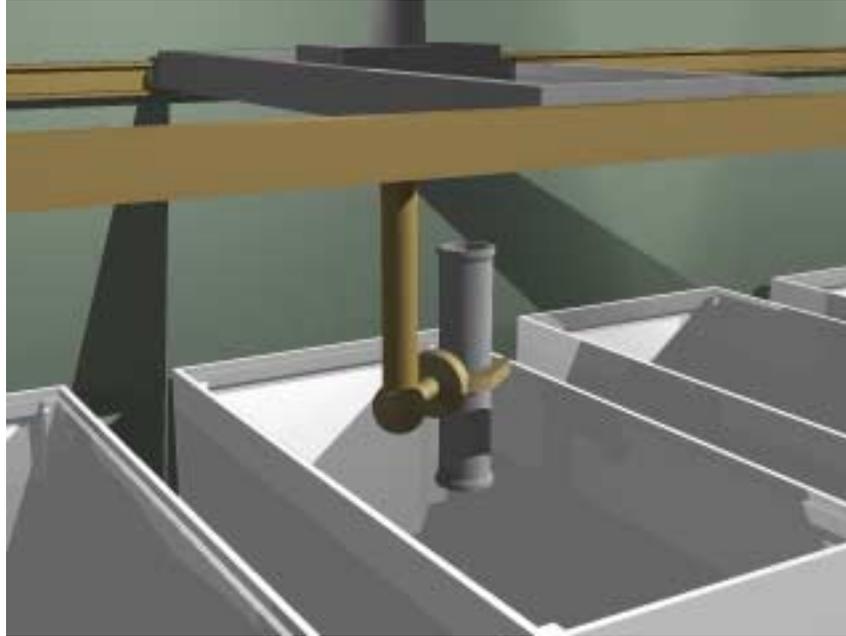


Figure 2. Conceptual low profile z-mast (to be designed) for operation in a trailer.

The potential benefits of this task include reducing personnel radiation exposure through robotic waste packaging, integrating with the waste characterization system to accurately manifest waste containers, and minimizing the number of waste containers required for a given volume of waste.

TASK DESCRIPTION

Background

The RWPS is coordinating its research with the INEEL Robotics HANDS-55 project, and will initially use their base material handling design to prove-out that aspect of the RWPS. During FY 2000, the HANDS-55 system was enhanced with a gripper, three joint arms, and a low-profile z-mast, and the preliminary design of a vision system for the RWPS was completed. This software will use depth, color, and edge detection to discriminate overlapping/adjacent objects specified by an operator. Also completed in FY 2000, was the first phase to developing a real-time packaging algorithm, based on information generated from the WCSS and seen with the vision system being developed.

Subtasks

The work to be completed for this task was separated into the following subtasks:

- Optimal packaging work with the University of Utah (USU) to establish basic algorithms and create a simulation of the “on-the-fly” packaging process
- XYZ system assembly
- Vision system development

- RWPS integration of XYZ and Vision systems and conduct the integrated test.

Need for RWPS

The DOE weapons complex has been transitioning from production to environmental restoration mode. In the process they have identified surplus facilities that must be decommissioned.

Although industry can successfully perform D&D operations with a variety of baseline techniques, present techniques are labor intensive, extremely costly, and result in considerable volumes of waste. For example, the amount of radioactive waste expected to be generated during the decontamination, decommissioning, and remediation of DOE's nuclear and associated facilities is significant. This waste, and its subsequent disposal, will have a direct impact on the operational costs associated with the D&D operations of these facilities. The DOE and other commercial D&D liability-holders require new and improved technologies with significant cost and safety improvements.

The INEEL has recognized these needs and taken an aggressive role in integrating its D&D operations with its applied engineering expertise. This integration allows INEEL facilities to be used as test beds for evaluating, demonstrating, and deploying innovative D&D technologies that generate less secondary waste, cost less, require less labor, reduce exposure of personnel to radioactive and hazardous materials, and improve safety for workers and the environment.

Fully implementing this task will diminish the need for long-term monitoring by allowing more cost-effective cleanup and removal of contaminated sites, thus reducing the number of facilities requiring long-term stewardship.

EM end users include the INEEL Facilities Deactivation Department that conducts the D&D activities at the INEEL. Representatives from this group as well as the department manager have been involved in reviewing this technology and giving ideas on needed improvements. They have continued to express an interest in using the system (and a willingness to demonstrate it) once it is completed.

Possible Future Activities

The following potential future activities are being pursued:

- RWPS, which is included in a proposal for the EM-50 funded Large Scale Demonstration and Deployment projects. The award of these proposals is to be announced December 2000.
- Ongoing discussions with Electric Power Research Institute to deploy new D&D technologies at Rancho Seco, such as RWPS. An unsolicited proposal was prepared and submitted to the National Energy Technology Laboratory in October 2000.

ACCOMPLISHMENTS

FY 2000 accomplishments included the following:

- The XYZ system design was completed and hardware for the XYZ system (3-joint manipulator and other parts) was ordered.
- A general purpose capitol equipment request was completed for a trailer to house the RWPS for transportation to and deployment at D&D sites.

REFERENCES

None

Environmental Separations and Barriers

Controlling Hazardous Environmental Chemicals By Developing Membranes for Chemical Separations and Barriers

Eric S. Peterson, Fred F. Stewart, Mason K. Harrup, Mark L. Stone, and Thomas A. Luther

SUMMARY

A major aspect of environmental management is being able to control chemical movement; this includes being able to (a) separate chemicals from one another, such as in removing contaminants from water, and (b) prevent the movement of chemical contaminants out of storage areas. For this reason, polymer membranes are important for long-term stewardship of such waste, because they can be developed to either separate contaminants from liquids, thus reducing the volume of waste to be handled, or form impermeable barriers to prevent chemical movements.

The use of polymer membranes in chemical separations is a promising technical area experiencing rapid advancements. Even so, a detailed understanding of chemical separations processes and what drives and controls them is fragmented at best. Historically, membrane separations research was focused on gas transport and separations, giving the areas of condensable gases, vapors, and liquids lower priority. However, liquid separations technology capable of functioning in harsh environments is urgently needed by both the DOE and industry. Early polymer membranes did not have the chemical and thermal stability to meet this need, but the development of newer materials is rapidly overcoming this problem. And even with the newer materials, only a few programs are focusing on polymer-based liquid separations membranes for harsh DOE- and industry-type environments. Previously, the INEEL has completed a variety of highly successful programs on various separations schemes under the sponsorship of both government and commercial sectors, but they have had very little sponsorship directed toward developing critical polymer membranes capable of functioning in harsh liquid chemical and ionic environments. The goal of this task is to focus on the separations technologies needed for these DOE applications.

The work for this task is divided into three subtasks; each is critical, and all are mutually complementary in meeting DOE's waste separations needs: (1) materials development for solid-phase selective-metal ion removal, (2) membrane development for high flux efficient separations, and (3) barrier development.

Materials Development for Solid-phase Selective Metal Ion Removal ("Atomic Tweezers") (Subtask 1)

Both DOE and industry need efficient methods for removing specific metal ions from solutions that possess high background concentrations of interfering ions without using mobile organic phases (solvent extraction). Our current research specifically addresses this need by using novel solid-phase selective extractants, thereby eliminating the need for organic solvents that are typically toxic, expensive, create numerous disposal issues, and may also reduce chelate/ion specificity. To date, the INEEL has developed a set of proprietary materials that provide selective copper concentration in the presence of high concentrations of iron. The most critical intellectual property involved has been the subject of two invention disclosure records, already elected to patent title (DOE Case No. S-91,266; LIT-PI-470, and DOE Case No. S-93,273; LIT-PI-573), two invited presentations, and one peer reviewed paper describing the materials resulted during FY 2000 (see Appendix A).

Membrane Development for High Flux Efficient Separations (Subtask 2)

Both DOE and industry need to control and remove organic contaminants from groundwater and aqueous waste streams. This subtask focuses on developing highly durable and chemically resistant membranes for reverse osmosis applications. Current reverse osmosis (RO) technology offers good throughput with little chemoselectivity. The challenges for this subtask are to combine the chemoselective nature of pervaporation membranes with the throughput efficiency of RO, and to significantly reduce the cost of phosphazene polymers by evaluating the use of a unique synthetic method developed at the University of Vermont. The work on this subtask has resulted in an invited paper presentation at a national society meeting, a patent, and a nomination for a Presidential Green Chemistry Award for the environmentally friendly synthetic pathway that has been discovered (see Appendix A).

Barrier Characterization (Subtask 3)

Barriers will be used as one of the prime technologies to stop present problem sites from growing larger and to prevent future contamination. Because polymer layers will be used in many barrier systems, there is an urgent need to characterize the candidate materials. Membrane introduction mass spectrometry (MIMS) is a sensitive analytical method that will be used to test the abilities of present membrane films to prevent permeations of typical waste plume chemicals. In addition to currently used materials, other films will also be tested to determine if improved formulations can be developed. This task has already resulted in two presentations and two peer reviewed journal articles (see Appendix A).

TASK DESCRIPTION

The goal of this task is to further EM's mission by developing cost effective methods for long-term monitoring and surveillance, developing methods to support the integration of land management with long-term stewardship, and find engineering solutions for permanent control of residual contamination and waste left in place. This task focuses on separations technologies needed for DOE applications. The work for this task is divided into three subtasks; each is critical, each relies on the other's data and synthetic know-how to be completed, and all three are mutually complementary in meeting DOE's waste separations needs, even though they appear to be discrete subtasks.

Materials Development for Solid-phase Selective Metal Ion Removal (Subtask 1)

Both DOE and industry need efficient methods for removing specific metal ions from solutions that possess high background concentrations of interfering ions without using mobile organic phases (solvent extraction). Our current research specifically addresses this need by using novel solid-phase selective extractants, thereby eliminating the need for organic solvents that are typically toxic, expensive, create numerous disposal issues, and may also reduce chelate/ion specificity. These solid-phase extractants solve another major problem with current technology by obviating unavoidable losses from the volatile organic solvent, which is both expensive and environmentally unacceptable. Initial results from our efforts to synthesize a commercially viable solid-phase extractant are very promising. To date, the INEEL has developed a set of proprietary materials that provide selective copper concentration in the presence of high concentrations of iron. The fundamental synthetic routes to these materials have already been established, and attachment to solid supports achieved in an efficient manner. The most critical intellectual property involved has been the subject of two invention disclosure records, already elected to patent title

(DOE Case No. S-91,266; LIT-PI-470, and DOE Case No. S-93,273; LIT-PI-573). However, additional development of these materials is needed to optimize efficiency and to resolve some problematic issues.

Novel solid-phase extractants will be synthesized that possess a high degree of specificity for copper in the presence of iron and other interfering ions. Our synthetic strategy will employ the third-generation route—based upon the Mitsunobu coupling—combined with the cyclization self-protection strategy for the isoxazazole already developed. Both possible coupling orders will be explored to determine which is the most effective. These new “head and tether” species will be fully characterized by nuclear magnetic resonance spectroscopy and other appropriate techniques. They will then be covalently attached to silica gel to render the final solid-phase product. If resources permit, these solid materials will be evaluated in column tests against a challenge solution to obtain selectivity and capacity data. Three tasks are being worked to develop this technology:

Task 1: Head and Tether Synthesis. An benzisoxazole “head” group will be synthesized and purified. This will then be coupled to an aliphatic “tether” via the Mitsunobu route. This product will be purified and fully characterized.

Task 2: Solid-phase Material Synthesis. The “head and tether” species generated in Task 1 will be attached to the surface of silica particles to form the novel solid-phase material. This product will be isolated and fully characterized.

Task 3: Preliminary Testing. As resources permit, data will be collected from both batch and column experiments using the solid materials from Task 2 versus the appropriate challenge solutions.

Membrane Development for High Flux Efficient Separations (Subtask 2)

Both DOE and industry need to control and remove organic contaminants from groundwater and aqueous waste streams. To meet this challenge, new materials need to be developed and characterized. This work will concentrate on the development of highly durable and chemically resistant membranes for RO applications. Phosphazene polymers, which have a higher level of chemical and thermal resistance than commonly employed organic polymers, are significant to developing new membranes. The INEEL has a well-established polymer and membrane research group that is ideally positioned to take advantage of this technology in creating new separations systems. Current technology in the field of RO offer good throughput with little chemoselectivity. The driving force behind this process is size exclusion—using “molecular sieving” to allow the smallest molecule to pass through the membrane while retaining larger molecules. Routes for separations based on chemical affinity reside largely in the technique of pervaporation. In pervaporation, chemicals are separated based on their ability to diffuse through and evaporate from the membrane. The efficacy of these two processes are dictated by the solubility of the selected permeate and its vapor pressure. Pervaporation, however, has two disadvantages; flux rates and energy requirements. Pervaporation, in general, is characterized by lower fluxes than RO, that often reduce the economic benefits of membrane processes. Additionally, the energy requirements for pervaporation are higher than for RO. The challenge of this work is to combine the chemoselective nature of pervaporation membranes with the throughput efficiency of RO, and to significantly reduce the cost of phosphazene polymers by evaluating the use of a unique synthetic method developed at the University of Vermont. Four tasks are being performed to develop this technology:

Task 1. Select appropriate phosphazene materials and membrane formation.

Task 2. Test new polymer membranes in reverse osmosis separations with aqueous feeds of common organic (methanol, ethanol) and inorganic species (sodium chloride).

Task 3. Perform and evaluate membrane testing under a series of differential pressures across the membrane. This task will be done using pressurization of the feed and also through selected use of vacuum on the permeate side of the membrane.

Task 4. Economic evaluation and pilot synthetic studies for the new phosphazene polymer synthesis developed in collaboration with the University of Vermont.

Barrier Characterization (Subtask 3)

Barriers will be used as one of the prime technologies to stop present problem sites from growing larger and to prevent future contamination. Because polymer layers will be used in many barrier systems, there is an urgent need to characterize the candidate materials. MIMS is a sensitive analytical method that will be used to test the abilities of present membrane films to prevent permeations of typical waste plume chemicals. In addition to currently used materials, other films will also be tested to determine if improved formulations can be developed. Six tasks are being performed to develop this technology:

Task 1. Identify the types of materials now being used and those being considered as barrier materials. This will involve personal communications, books, and other literature search methods.

Task 2. Collect specimen amounts of the materials for testing.

Task 3. Manipulate the materials to produce thin films that are suitable for MIMS testing.

Task 4. Test the materials in a MIMS configuration against the four contaminants listed above.

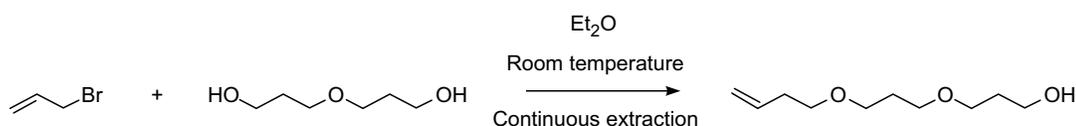
Task 5. Perform a limited number of gas barrier film tests.

Task 6. Report the results.

ACCOMPLISHMENTS

Materials Development for Solid-Phase Selective Metal Ion Removal (Subtask 1)

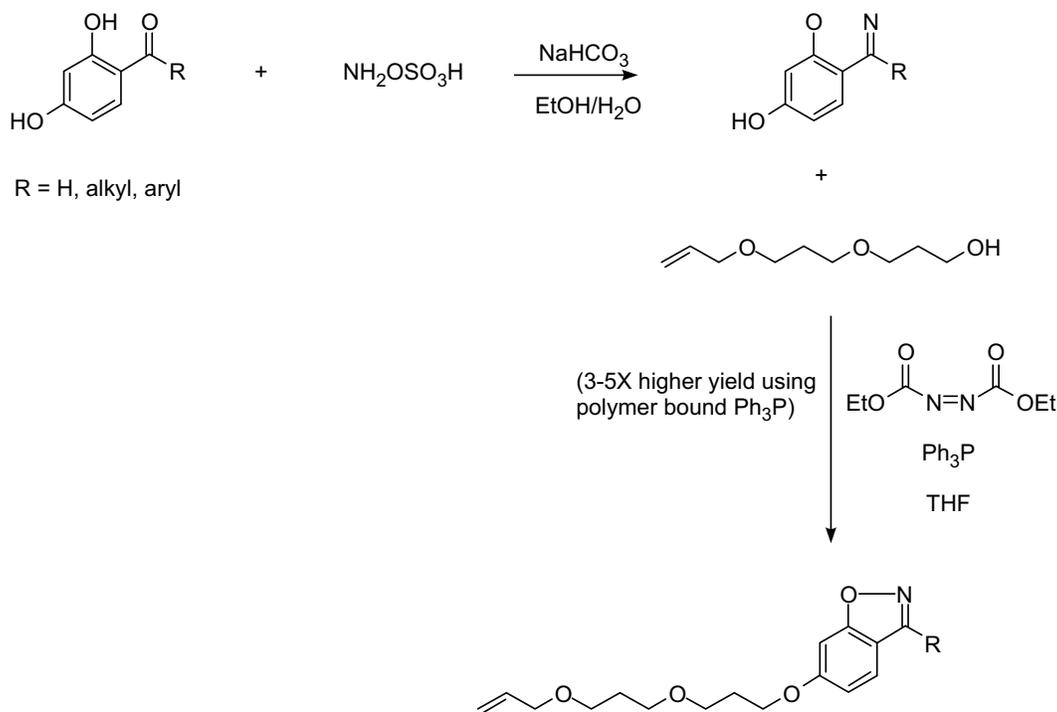
New syntheses have been performed to accomplish the initial goal of obtaining a purified “head and tether” specie with which to functionalize the surface of silica particles. To this end, a new tether was synthesized, one that improves upon the previous generation by possessing a more hydrophilic character which allow for better solvent (water) surface interactions; thus, speeding the kinetics of ion capture. The synthesis is shown below in Figure 1.



Gc00 0681

Figure 1. Synthetic scheme for the production of the hydrophilic tether.

The primary coupling reaction for attaching the “head” to the “tether” is the Mitsunobu ether reaction.³ This reaction was run in a homogeneous fashion, and while successful, the purification was problematic leading to lower than desired yields. To overcome this problem, a new reagent was employed that contained the triphenylphosphine as a surface functionalized polymeric material, allowing the reaction to proceed in a heterogeneous fashion. The subsequently produced by-product, triphenylphosphine oxide, is then easily removed by bulk filtration through a fritted glass funnel, greatly simplifying subsequent purification steps and thereby improving product yields, see Figure 2.



Ge00 0682

Figure 2. Synthetic scheme for attaching the tether to the head group.

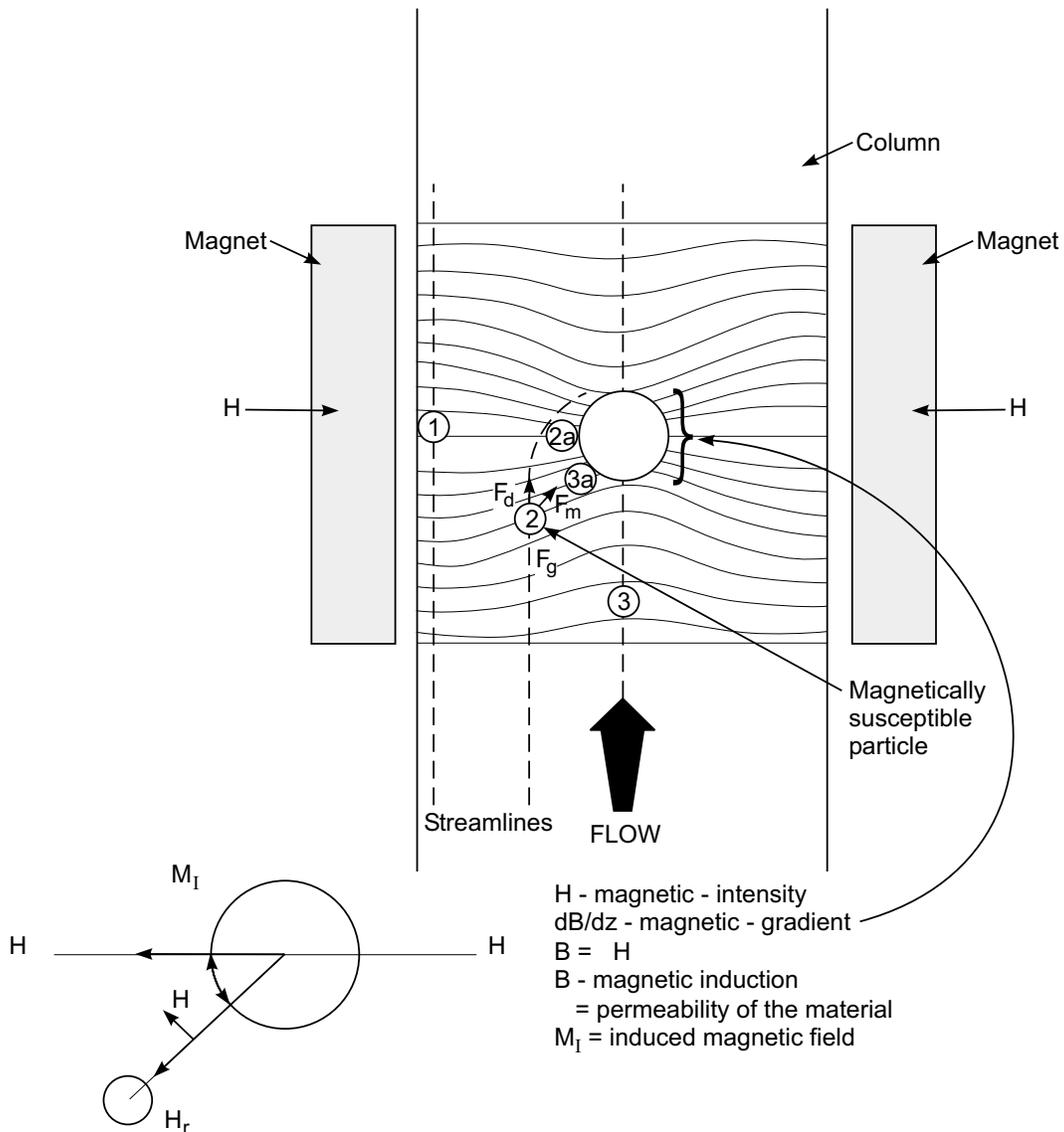
The final step in producing the deliverable product is the silylation of the olefinic tail for condensation onto the surface of the ceramic, which is the focus of our current synthetic efforts.

Magnetically Enhanced Filtration

For a theoretical focus, we significantly modified an existing theoretical treatment¹ of the influence of a magnetic field upon particle capture in a magnetically active column. In this activity the practical advancement that we sought to provide was the addition of a flow vector component to the previous model. This important expansion allows for prediction of column optimal performance in a “true to life” situation where a feed stream is being treated in a flowing column instead of a still batch-mode process.² The limiting assumption necessary to make this model tractable was that only one contaminant particle interacting with one column particle could be considered as a function of time and position.

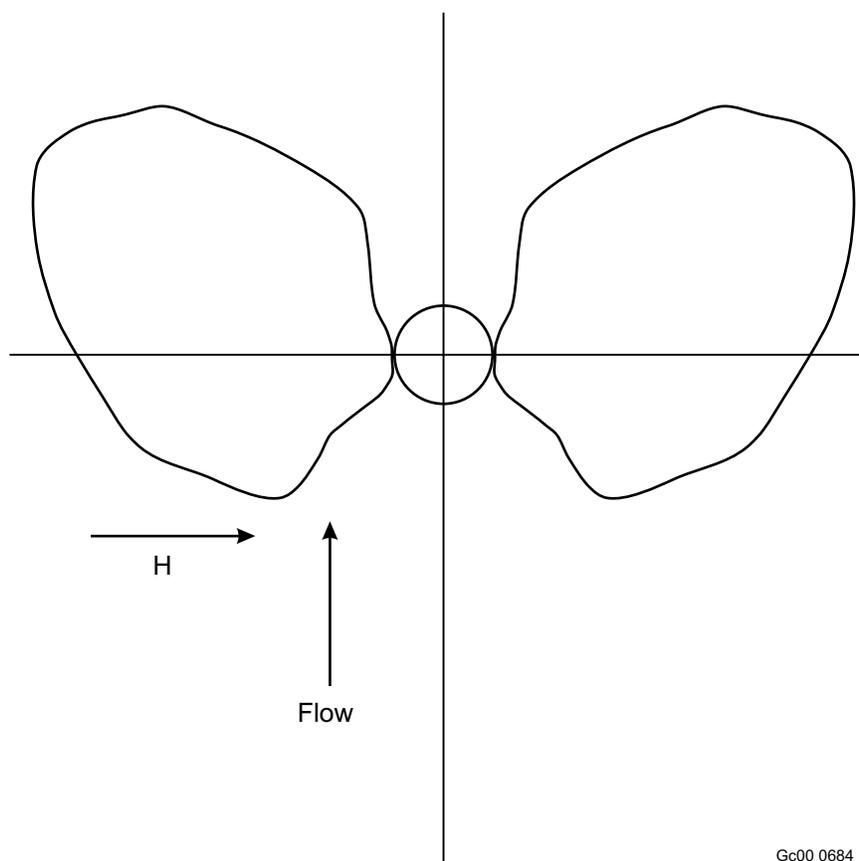
This model (see Figure 3) describes the magnetically enhanced separation system, a natural clash of forces: drag on the contaminant particle from the moving liquid feed stream resisting capture against

magnetic attractive forces between the contaminant particle and the column bed material inducing capture. From this fundamental clash, three differing potential interactions are predicted as depicted in Figure 3. In path one, extreme distance between the contaminant and the bed pack lead to no interaction and hence no capture. Conversely, in path three, direct collision ensures capture. The dominant and defining path, path two, considers the balance of forces when a contaminant particle comes within the “sphere” of influence of the bed particle. The net result is that, although the magnetic force is theoretically spherically distributed about the bed particle, factoring in Brownian motion and a flow component vector significantly alter this shape as shown in Figure 4. In Figure 4, the bed particle is shown as an ideal sphere and the line drawn around this particle is where the balance of forces, defined very simply (here) as $F_{\text{capture}}/F_{\text{escape}} = 1.0$. Within this boundary, capture should occur, while outside escape should occur.



Ge00 0683

Figure 3. Representation of the three potential particle paths through a magnetic separator.



Gc00 0684

Figure 4. Graphical representation of the limiting radius of capture in a theoretical system. The line represents the boundary where $F_{\text{capture}}/F_{\text{escape}} = 1.0$.

Magnetically Enhanced Filtration Experimental Work

Physical experiments were performed on both diamagnetic (silica) nanoparticles and ferromagnetic, nonflocculating (magnetite encapsulated within polyacrylic acid) nanoparticles to determine the effects of flow velocity, the strength of the externally applied magnetic field, and complement existing data that was previously collected for paramagnetic nanoparticles. Column flow experiments were conducted on particles of various discrete size ranges to determine when the threshold of capture was achieved. These data were then correlated and compared to the results expected based on the above theoretical work from which we determined that the correlation between theory and experiment is surprisingly good (see Figure 5), which adds credibility to the validity of this theoretical model. It must be noted, however, that experimental data exhibits consistently poorer performance than is predicted by the model. This reduction in performance is due primarily to two factors: first, multiple particle systems have particle/particle physical impacts that would reduce capture efficiencies; and second, as the magnetite column particles are packed in a random orientation, the fields that they exhibit will have some regions of destructive overlap, reducing the effective magnetic field below the theoretical threshold in some areas of the column.

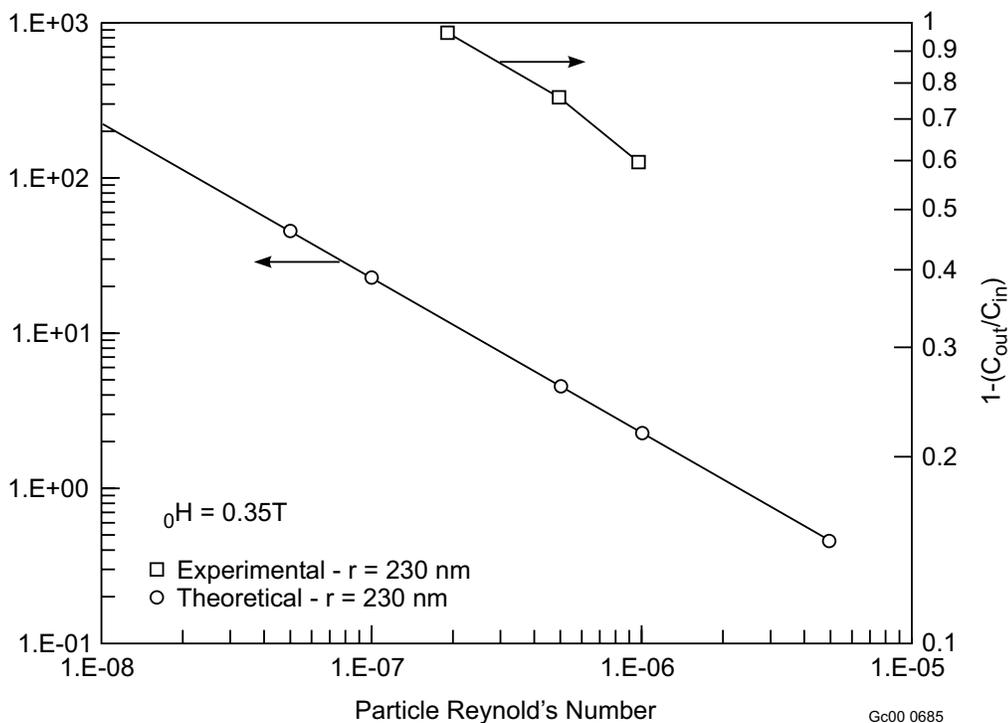


Figure 5. Graph of the correlation between experimental results and theoretical expectations in a magnetic separator (230 nm paramagnetic particles at a magnetic strength of 0.35 T).

Membrane Development for High Flux Efficient Separations (Subtask 2)

Task 1, "Selection of appropriate phosphazene materials and membrane formation," was put on hold due to lack of personnel.

Task 2, "Testing of new polymer membranes in reverse osmosis separations with aqueous feeds of common organic (methanol, ethanol) and inorganic species (sodium chloride)," was put on hold due to lack of personnel.

Task 3, "Perform and evaluate membrane testing under a series of differential pressures across the membrane," was put on hold due to lack of personnel.

Task 4, "Economic evaluation and pilot synthetic studies for the new phosphazene polymer synthesis developed in collaboration with University of Vermont," is being executed. The synthetic process (see Figure 6) is designated as the "New Process." This task has resulted in signature of a nondisclosure agreement with Technically, Inc., of Woburn Massachusetts. A contract for performance of the pilot-scale synthesis studies coupled with execution of an economic evaluation of the process has been issued. Technically, Inc., has signed the contract, and work is to begin during the month of October 2000.

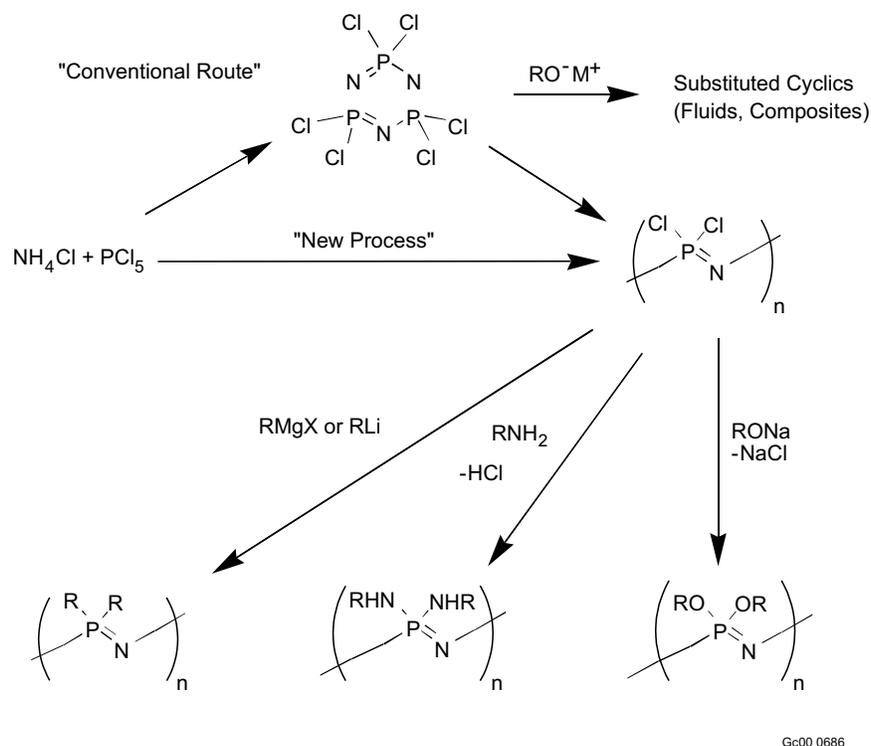


Figure 6. Synthetic Scheme for the new phosphazene polymer synthesis.

Barrier Characterization (Subtask 3)

The purpose of this subtask was to evaluate the use of MIMS as a tool to determine if different materials could be effective barriers for DOE waste containment applications. The approach was to obtain a partial list of the types of materials used as barriers and pond liners, obtain representative samples of these classes of materials, and to use MIMS to determine the permeability's of analytes that might be present in subsurface contamination plumes.

There are many types of barriers that are needed in different applications. Very general categories of barriers include air sparging walls of water, cement walls, grouted barriers, clay fillers, reactive permeable barriers (amorphous ferric oxyhydroxides and other zero valent iron systems), and a wide variety of polymer sheets or films. The list of polymers includes urethanes, polyethylene, linear low density polyethylene, polypropylene, polystyrene, polyvinylchloride, vinylesters, and many other elastomers such as ethylene propylene diene monomer (EPDM) rubber. Only the materials that can be formed into thin films are suitable for MIMS analysis. This includes all of the polymeric materials.

Our primary objective was to evaluate MIMS as an analytical for determination of permeabilities for potential barrier materials. A Varian Saturn II gas chromatograph (GC)/mass spectrometer has been modified by removing the GC and replacing it with a special valve, port, and probe assembly, (see Figure 7). The probe is a commercial unit that has an integrated pump and heater system specifically designed for MIMS. The system flows a pure solvent (water) stream across the membrane at a constant rate (e.g., 1 mL/min). There is an injection port, into which a 1 ml slug of the test solution is inserted into the feed system. The slug of material passes across the membrane and then exits to a collection unit. Figure 8 shows how the membrane is attached to the tip of the probe that is inserted into the spectrometer.

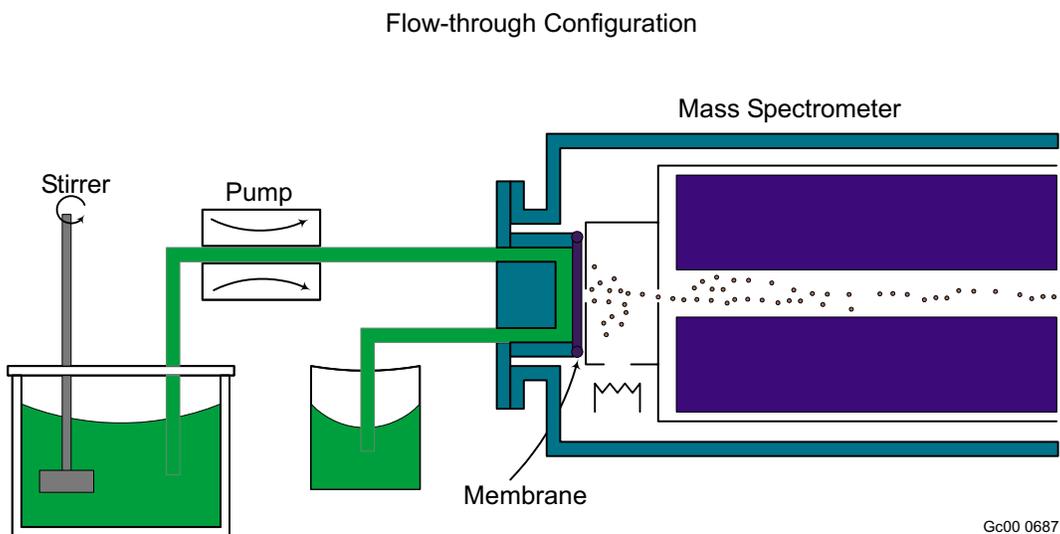


Figure 7. Sheet membrane MIMS probe.

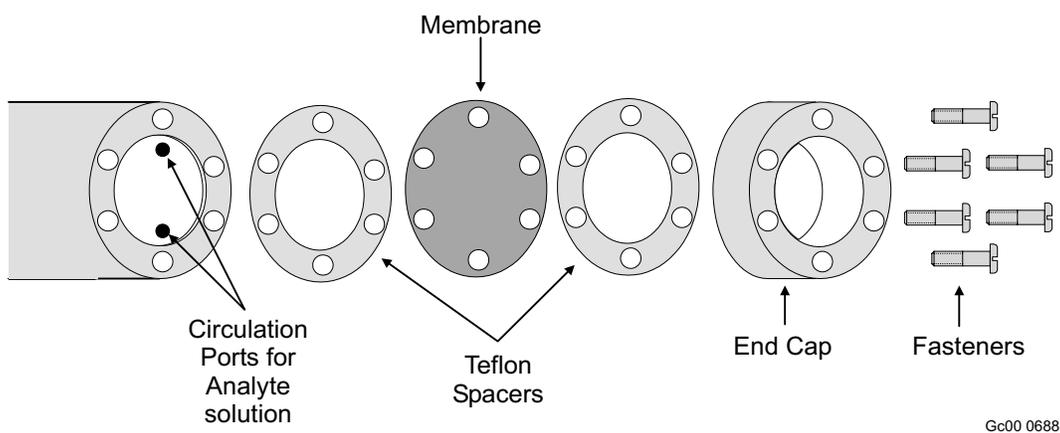


Figure 8. Illustration showing how the membrane is attached to the probe.

MIMS can be an extremely sensitive analytic technique. Several authors have reported parts per billion detection limits; there are some who have reported parts per quadrillion detection of organics in water. The membrane does the separation so the only sample preparation is filtering enough so that one has a nonclogging fluid that can be pumped across the membrane. In addition to the ultimate sensitivity of the technique another benefit is the detection range. It is not uncommon to be able to make measurements over five or six orders of magnitude without making any system changes.

The primary driver in the development of the MIMS technique is to develop improved analytical detection methodologies and detection limits of the desired analytes. The strength of MIMS resides in its ability to allow the transfer of volatile and semivolatile compounds from aqueous solution or other matrices to the gas phase with good efficiency. The transfer involves the adsorption of the analyte onto the membrane followed by diffusion across the membrane and into the vacuum, thus providing some

degree of enrichment. As researchers develop new materials that are designed for use as subsurface barriers, MIMS can be used to determine how permeable they are to the target chemicals.

The long range goals of the task were divided into two logical components: test existing barrier films, and correlate structure and function (build a database). This program will benefit greatly by leveraging past programs in which many new polymers have been produced.

Table 1 summarizes the data obtained from the MIMS experiments in which four chlorinated hydrocarbons (trichloroethylene TCE, methylene chloride MeCl_2 , chloroform, and carbon tetrachloride) were used against five different polymers.

MIMS appears to be well-suited for the kind of testing needed to characterize film/sheet materials as potential barriers. The mass spectrometer (the detector for the system) is extremely sensitive. The main drawbacks to using the MIMS technology for this kind of evaluation is that it is not very portable and the ion trap type of spectrometer that we are using is not well suited to films that have high water permeation rates. Literature reports suggest that one can manage water better using quadrupole mass spectrometers.

Table 1. Comparison of MIMS experiments and polymers.

Polymer	TCE	Methylene Chloride	Carbontetra chloride	Chloroform
EPDM (thick) ^a	20 ppm	200	>200 ppm ^c	>200 ppm
Neoprene (thick) ^a	>200 ppm	>200 ppm	>200 ppm	>200 ppm
EPDM (thin) ^b	200 ppb	20 ppm	Too noisy	20 ppm
Neoprene (thin) ^b	>200 ppm	>200 ppm	>200 ppm	>200 ppm
Polyvinylidene chloride	20 ppm	>200 ppm	>200 ppm	200 ppm

a. The thick films are membranes cast in thicknesses such that they were self supporting, on the order of 100 to 200 μm thick.

b. The thin films were made by painting a thin coating of a solvent containing the polymer onto the surface of a microporous support layer.

c. The concentration of the analytes used in this test started at 200 ppm and then if peaks were observed the concentrations were reduced by a factor of ten until no peaks were observed. If no peak was observed at the 200 ppm level then that is designated in the table as >200 ppm.

REFERENCES

1. A. D. Ebner, J. A. Ritter, and H. J. Ploehn, "Feasibility and Limitations of Nanolevel High Gradient Magnetic Separation," *Separation and Purification Technology*, Vol. 11, 1997, pp. 199–210.
2. G. B. Cotton and H. B. Eldridge, "Nanolevel Magnetic Separation Model Considering Flow Limitations," *Chemical Engineering Science*, Submitted.
3. J. March, "Advanced Organic Chemistry—Reactions, Mechanisms, and Structure," 4th ed., *Wiley Interscience*, New York, 1992.

Proton Conducting Ceramic Membrane Applied to Spent Nuclear Fuel Stewardship

Removing Water and Hydrogen from Spent Nuclear Fuel

Paul A. Lessing (INEEL); Yang-Ki Hong (University of Idaho);
Shekar Balagopal (Ceramatec, Inc.); Rainer Gadow (University of Stuttgart, Germany)

SUMMARY

Part of EM's mission is to reduce high level waste and place it all in one long-term dry storage facility at Yucca Mountain, Nevada. New regulations for Yucca Mountain, however, allow for only a very small amount of total water to be present in any large canisters to be placed there. This is a problem for high level waste such as spent nuclear fuel, which contains more water than will be allowed. In addition, some of that water is chemically bound to the waste, making it much more difficult to remove. The current method to remove this water is with high temperature calcination, a process that would require the installation of large, expensive equipment at many DOE sites.

The objective of this research is to develop a unique ceramic membrane that will transport hydrogen or water, or both, at relatively low temperatures (e.g., 100–300°C) in response to chemical and electrical potential differences. Successful completion of the research will offer a method to enable packaging of damaged or corroded spent nuclear fuel or high-level waste that contains excessive levels of water (especially chemically bound water).¹ Hydrogen in canisters is the result of water radiolysis or the reaction of water with uranium or other internal canister materials. When developed, the membrane will permit gaseous water or hydrogen, or both, to escape from the package while completely retaining back-filled helium, radioactive decay gases, radioactive particulate, and oxygen. This will enable compliance with shipping regulations and proposed storage regulations (e.g., draft Waste Acceptance System Requirements Document, DOE/RW-0351), which allow for only very small amounts of total water (e.g., 200 g) to be present in large canisters.²

We are conducting the research in cooperation with the University of Idaho and the University of Stuttgart, Germany, and a small high-technology ceramics company, Ceramatec, Inc. The University of Stuttgart and Ceramatec are developing new experimental ceramic electrolytes. The INEEL is directing the work and conducting direct current (dc) performance testing of the resulting cells. The University of Stuttgart has developed special compositions of potassium beta" (β'')-alumina that can be proton-exchanged without cracking the electrolytes. The proton-exchange process, however, appears to selectively leach out a phase within the ceramic such that the material no longer is gas-tight. Ceramatec is developing a type of NASICON ceramic (PRO-NAS) that can be proton-exchanged while remaining gas-tight. Both types of ceramics exhibit relatively high conductivity at low temperatures when measured using complex impedance techniques. However, proton conductivity (related to hydrogen flux) has not been measured in practical dc cells for either type of electrolyte. In this research, dc tests will be conducted at the INEEL to measure hydrogen and water transport properties of the electrolyte material. The testing will differentiate the type of hydrogen bonding and transport mechanisms within the crystal structure of the two types of ceramics. The results will be published in a national journal specializing in electrochemistry or ionic conducting solids. The dc testing requires development of well-adhering electrodes of high hydrogen solubility. The University of Idaho is developing sputtering technology to apply suitable palladium/silver electrodes. The electrode work is innovative and will be published in a suitable journal jointly by INEEL and University of Idaho scientists.

To date, the task is only partially complete. We received electrolytes from the University of Stuttgart, and measurements indicated that these proton-exchanged ceramics were not gas-tight. We have started efforts to improve the density and concurrently forge on bonded electrodes, and have designed and constructed electrolyte testing and proton-exchange apparatus at the INEEL. Subcontracts were established with the University of Idaho and Ceramtec, and work has begun. Two monthly reports from the University of Idaho indicate good progress on sputtered electrodes (using University of Stuttgart electrolytes). We received an engineering design report from Ceramtec, and they have delivered their first batch of electrolytes. We will begin dc testing here after application of suitable electrodes.

TASK DESCRIPTION

Figure 1 shows a schematic of two different hydrogen conducting membranes that we have proposed using to relieve hydrogen pressure in DOE canisters. The *passive* design at the left is a Pd/Cu metal alloy membrane that is starting to become available (for high temperature hydrogen separation) from commercial sources. It is strictly a temperature-activated, pressure-driven process; high-hydrogen fluxes are measured at elevated pressures and temperatures. The charged INEEL design at the right is the subject of this task. The ceramic membrane also conducts via activated pressure-driven processes. However, since the ceramic is a dielectric (does not conduct electrons), the flux can also be increased by applying a dc voltage (electrical gradient) across the electrolyte that drives the charged protons. Therefore, the ceramic membrane (with appropriate electrodes) conducts hydrogen in response to both pressure and applied dc voltage (e.g., battery).

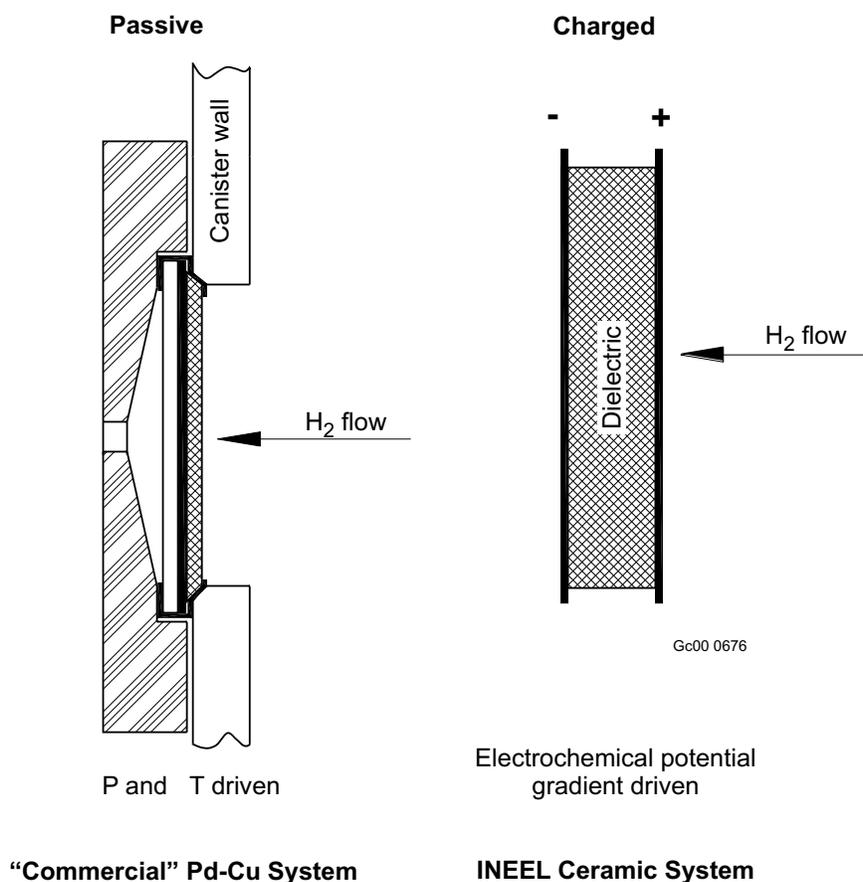


Figure 1. Schematics of hydrogen-conducting membrane concepts.

Without an applied dc voltage, the ceramic membrane (with electrodes) will still transport hydrogen in response to a pressure differential. However, for the transport to continue under pressure-only conditions, the anode must be electrically connected (shorted) to the cathode. Otherwise, electrode polarization (build up of electrons) will occur and stop the process.

The INEEL ceramic design has the advantage of allowing the device to be operated at lower temperatures (depending on specific composition of the membrane), and it can remove the hydrogen down to extremely low equilibrium levels, as determined by the Nernst³ equation applied at equilibrium. The appropriate Nernst relationship is given in Equation (1):

$$V = RT/nF [\ln (PH_2^{\text{II}} / PH_2^{\text{I}})] \quad (1)$$

where

- V = a applied voltage
- n = number of electrons transferred (2) per hydrogen molecule during the reduction reaction
- R = universal gas constant
- T = absolute temperature
- F = Faraday's constant
- PH_2^{II} = partial pressure of hydrogen on canister side of cell
- PH_2^{I} = partial pressure of hydrogen on the atmospheric side of the cell.

Water vapor might also be removed, depending on the type of hydrogen bonding and conduction mechanisms occurring within the ceramic.⁴ For instance, one type of bonding can be H₂O molecules associated with protons as hydronium ions with hydrogen bonds. This bonding is known for beta-alumina type ceramics.⁵ Another type of bonding could consist of a proton bound to an oxygen ion of the ceramic lattice; conduction arises from the proton hopping along adjacent oxygen ions (also can be present in beta-alumina).⁶ Different fluxes of hydrogen gas or water vapor will result from varying the water vapor content (partial pressure) of the pressurized (up stream/canister) gas atmosphere. Heating to excessively high temperatures dehydrates the ceramic (if it is primarily a hydronium conductor) and can also drive out bound protons. This destroys the ionic conductivity and may also fracture the ceramic membrane. Rehydration or protonation may occur reversibly at lower temperatures (in water vapor or hydrogen containing atmospheres) but would be pointless if the membrane has been cracked or is irreversible because the basic crystal structure has changed (collapsed).

Performance measures for the proton-conducting ceramic membranes are that the cell must be hermetic (leak-tight), and the hydrogen flux must be a function of temperature, hydrogen pressure (from a canister), and applied voltage. The total available hydrogen flux of a cell must be sufficiently high to relieve gas pressure within a canister before it reaches an unacceptable level. Of course, the total flux of a cell increases with total cell surface area, operation temperature, gas pressure, and applied voltage. A reasonable (e.g., 100- to 500-cm²) maximum cell area will have to be specified. A worst-case estimate for a hydrogen generation rate in a spent fuel canister would be from water's reaction (oxidation) with uranium metal. An estimate of the rate of uranium metal consumption is 647 mg U/cm²/yr at 40°C. The surface area of uranium for spent Advanced Test Reactor fuel (a high surface area type of fuel) in a certain canister has been estimated at 86.3 × 10⁴ cm². Multiplication results in a worst-case estimated generation rate (maximum) of 0.536 mole/h or 12.01 L/h (200.17 scc/min) of hydrogen gas.⁷ Therefore, a cell must transport approximately 200 scc/min through an area of approximately 500 cm², using an

applied voltage that does not decompose the ceramic (e.g., less than 2 volts). This translates to a minimum goal for hydrogen transport across a ceramic membrane (in a cell) to be about 4.0×10^{-1} scc/min-cm² at temperatures and internal pressures that are reasonable for a given canister (e.g., 100°C and 100 psig). The hydrogen generation rate, temperature, and pressure will vary, depending on the internal physical and chemical situation of the canister being addressed.

We expect the Ceramatec membrane (PRO-NAS) to conduct better than the German (H-β⁻-alumina) at the low temperature extreme of the test range, but to be less chemically stable than the German membrane at the high temperature extreme of the test range. Membrane performance characteristics will be compared to various spent fuel and waste container hydrogen generation situations. If the flux numbers are encouraging, we will seek further funding from a variety of sources to develop a prototype device. This would include discussions, presentations, and proposals to the various groups charged with the storage and transportation of spent nuclear fuels and wastes that contain water and generate hydrogen. Design of the housing assembly and dc power source (if necessary) would depend on the application of the specific canister.

ACCOMPLISHMENTS

We received a 17 page engineering design report (prepared specifically for the INEEL) from the University of Stuttgart on the preparation and physical and electrical characterization of their proton-exchanged β⁻-alumina.⁸ Their material exhibits relatively high proton conductivity when measured using alternating current (ac) complex impedance testing. These measurements were made using an ac impedance analyser (Zahner^a Model Im5d). For conductivity measurements, we sputtered the sample surfaces with Pt. The samples were mounted between two Pt plates and fixed within a quartz measurement cell. Applied voltage was 0.1 V. For all samples, frequency ranged from 1 Hz to 1 MHz. All measurements were taken in Ar atmosphere. The temperature was varied from room temperature up to 700°C for the K-β⁻-alumina and 400°C (to prevent dehydration) for H-β⁻-alumina, respectively. We calculated conductivity using nonlinear least square fit procedures to simulate the data. Figure 2 shows the ac conductivity data.

The critical step in manufacturing crack-free H-β⁻-alumina polycrystals is fabricating single-phased K-β⁻-alumina precursor material (K_{2.05}Mg_{0.35}Al_{10.65}O_{17.3}). After sintering dense single-phase polycrystalline K-β⁻-alumina bars, Hg-porosity measurements confirmed that the density (3.24 g/cm³) closely correlated (>95 %) with the theoretical density (3.42 g/cm³). Ion exchange was then easily performed in dilute acids, even at room temperature. Concentrated acids dissolved beta alumina completely, in total agreement with the well known amphoteric character of β-alumina itself. However, density tests and SEM measurements made at the INEEL show the density decreased to about 85% of theoretical after the proton-exchange step. The University of Stuttgart-IFKB attributed this to the presence of a second phase that was being leached out by the exchange process. This means the proton-exchanged membranes we received from the University of Stuttgart were not gas tight.

In response to the German situation, we identified Ceramatec, Inc., as a company that could provide a type of ceramic that could be successfully proton-exchanged. This material is proton-exchanged NASICON (PRO-NAS). PRO-NAS is an emerging material that was originally developed for ionic conduction in liquid solutions (rather than gases). It is chemically stable in both acidic and caustic conditions. Ceramatec has measured its proton conductivity to be 9.8×10^{-3} S/cm at 55°C in a liquid

a. Zahner GmbH, 96308 Kronach.

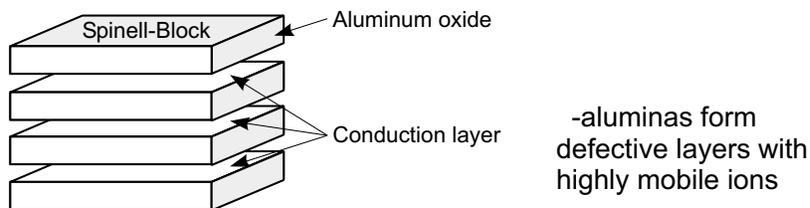
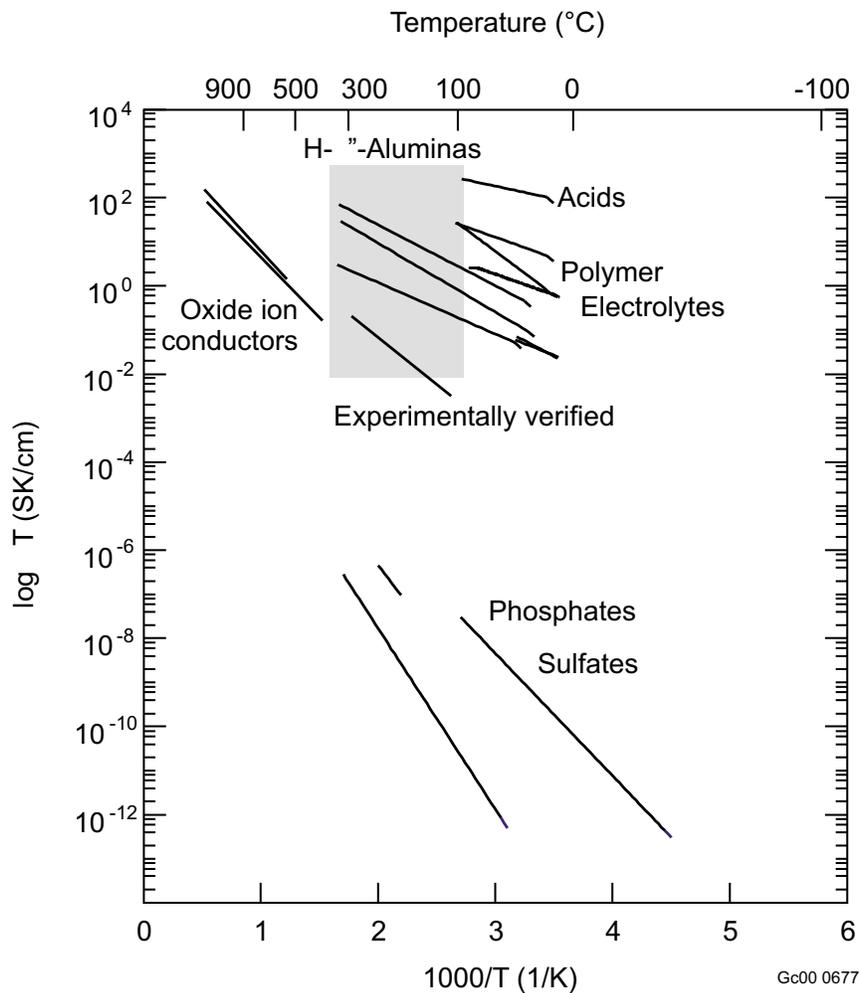


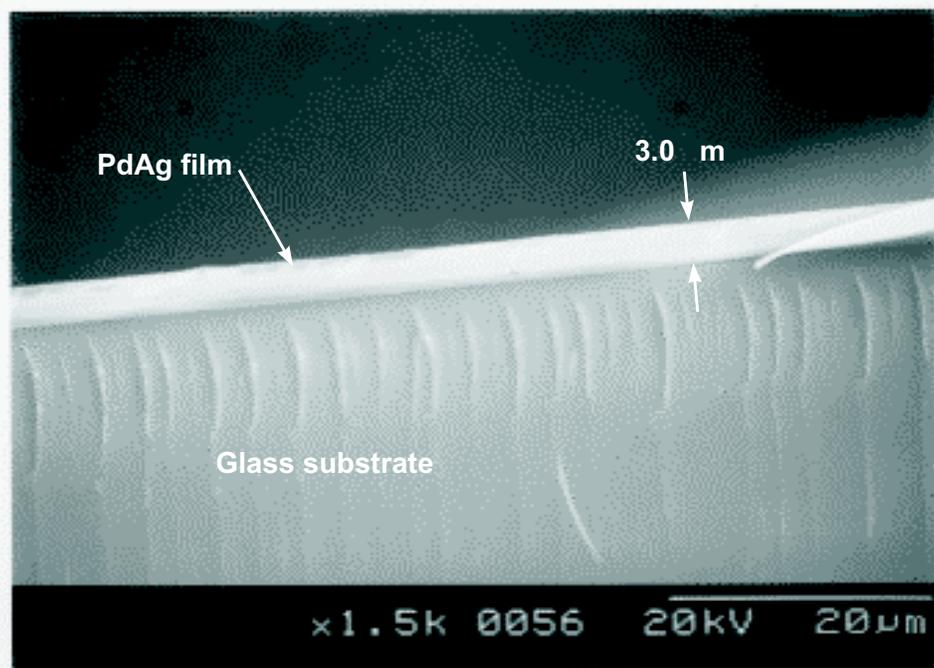
Figure 2. Conductivity of University of Stuttgart H-β⁻-alumina compared to other ionic conductors.

H₃PO₄ solution. Very few compositional or conductivity data are available for this proprietary material; however, an independent party reportedly measured PRO-NAS conductivity at 4×10^{-3} S/cm at 80°C in a H₂/O₂ cell (H₂ gas stream containing 3% H₂O). This indicates that PRO-NAS will conduct protons in a gaseous atmosphere (at temperatures lower than the H-β⁻-alumina), but we do not know if it is primarily a proton or a hydronium conductor. We will determine the relative contributions to the conductivity from the two possible species as part of our INEEL testing program by varying the moisture content of the hydrogen testing gas.

The University of Idaho has submitted two monthly progress reports. They have installed a substrate holder and substrate heater on their production-size sputtering unit and started deposition studies of Pd-25% Ag alloy. Figure 3 shows a SEM micrograph of Pd/Ag film produced at the university. Figure 4 shows the effect of substrate temperature on the x-ray diffraction pattern of the film. Observations to date revealed that (a) the as-deposited film crystallized without substrate heating, (b) a sputtering rate of about 200 nm/min could be achieved, (c) the (111) peak height decreased with increasing substrate temperature in the range of 25 to 450°C, and (d) the (111) peak shifted toward lower angle with substrate temperature. Optimization studies are now being conducted, including adhesion experiments.

Film: Glass/PdAg	
Sample	PS7
Target	Pd-25% Ag
Substrate Temperature	RT
Total Ar Pressure	5 mtorr
RF Power Density	1 W/cm ²
Sputtering time	15 min

Substrate: Corning glass



Sputtering rate under the given sputtering conditions: 200 nm/min

Gc00 0678

Figure 3. Palladium/silver alloy film sputter coated at the University of Idaho

Film: glass/PdAg						
Sample	PS7	PS4	PS5	PS6	PS8	PS9
Substrate Temperature (°C)	RT	200	315	400	429	450
RF Power Density	1 W/cm ²					
Sputtering time	15 min					
2 theta of (111) plane's peak	39.74	39.68	39.58	39.42	39.68	39.33

Substrate: Corning glass

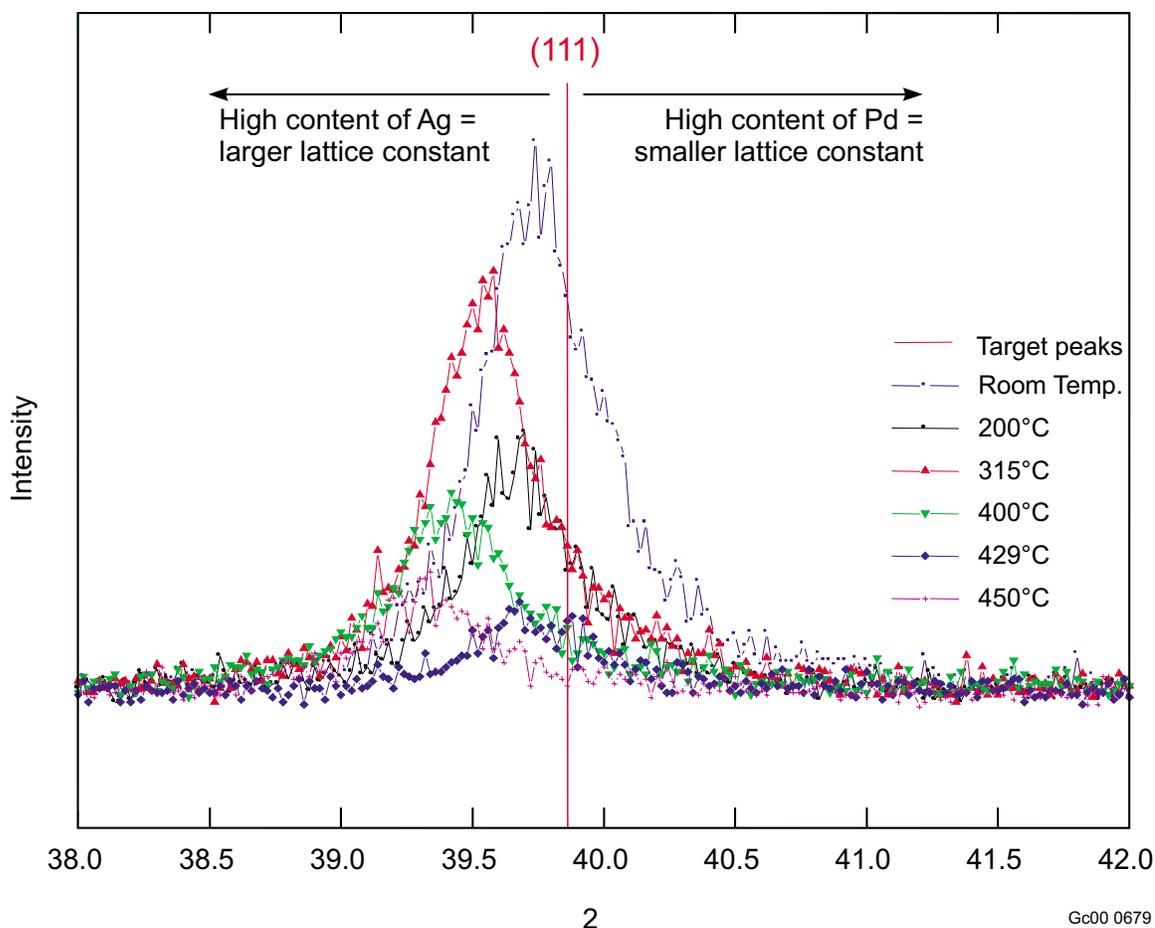
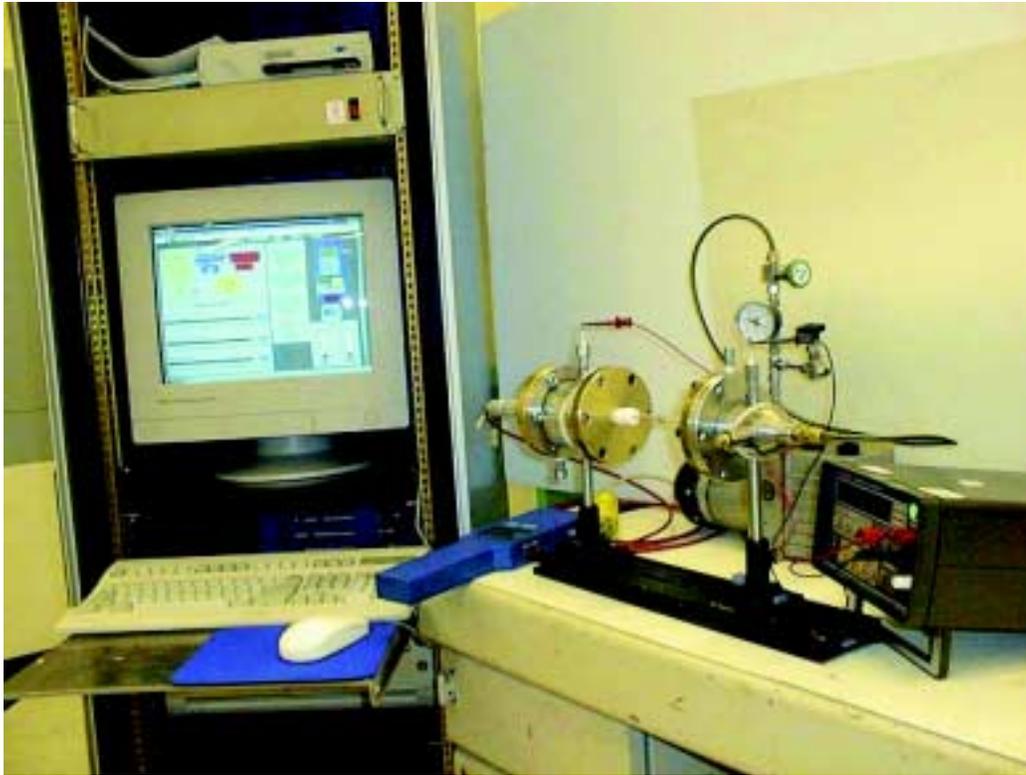


Figure 4. Shift of (111) peak with substrate deposition temperature.

The INEEL has completed fabrication of a dc cell testing apparatus, which builds the INEEL's experimental capabilities in this new area of research. Figure 5 shows the apparatus. A new Gamry Model PC4/750 Potentiostat/Galvanostat/Zero resistance ammeter instrument drives the dc cells. We can purchase additional software in the future to enable the instrument to be used to perform complex ac complex impedance tests. We conducted some work to hot isostatically forge dense, sheet Pd/Ag alloy electrode material onto the H-β"-alumina electrolytes. The idea was to strongly bond the electrodes while concurrently increasing the density of the electrolytes such that they would be gas-tight (without decomposing the crystal structure). This work has been put on hold due to budget limitations.



Gc00 0680

Figure 5. New hydrogen flux cell testing apparatus fabricated at the INEEL.

The task had the following product/deliverables:

- Sufficiently complete engineering test data that the basic feasibility of the membrane to function as a pressure relief system for a spent nuclear fuel canister can be determined.
- Periodic monthly progress reports, including detailed sample preparation data to National Spent Nuclear Fuel Program engineers. We do not plan to have the engineering test data from the hydrogen and water vapor flux measurements before February 2001.

REFERENCES

1. P. A. Lessing, "Effects of Water in Canisters Containing DOE Spent Nuclear Fuel," DOE/SNF/REP-017, Rev 0, United States Department of Energy, National Spent Nuclear Fuel Program, peer reviewed, October 1998.
2. P. A. Lessing, "Standard Guide for Dryness in Canisters Containing DOE Spent Nuclear Fuels," DOE/SNF/G-003, United States Department of Energy, National Spent Nuclear Fuel Program, Rev 0, peer reviewed, May 1999.
3. A. J. Bard and L. R. Faulkner, *Electrochemical Methods – Fundamentals and Applications*, John Wiley and Sons, 1980, pp. 51 and 100.
4. C. K. Kuo, A. Tan, P. Sarkar, and P. S. Nicolson, "Water Partial Pressure-dependent Conductance and Humidity Effects on Hydronium- β - Al_2O_3 Ceramics," *Solid State Ionics*, Vol. 58, 1992, pp. 311–314.
5. N. J. Dudney, J. B. Bates, and J. C. Wang, "Hydration of Lithium β -alumina," *J. Chem. Phys.*, 77, 1982, pp. 4857–4869.
6. G. C. Farrington, " H_2 and H_2O Oxidation at a Pt/ Na^+ -Beta Alumina Interface," *J. Electrochem Soc: Electrochemical Science and Technology*, 1976, pp. 833–834.
7. Paul A. Lessing, "Scientific Investigation Plan for Qualification of Palladium/Copper Membrane," Rev 0, Report DOE/SNF/PP-021, United States Department of Energy, National Spent Nuclear Fuel Program, peer reviewed, April 2000.
8. G. W. Schafer and R. Gadow, "Fabrication of H- β -alumina Polycrystals," special report prepared for the INEEL, University of Stuttgart, Institute for Fabrication of Ceramics (IFKB), Allmandring 5b, D-70569 Stuttgart, Germany.

Spectroscopic Investigations at Solid-Supercritical Fluid Interfaces in Support of Advanced Supercritical Separation Techniques

Advanced Environmental Separations Science for Remediation

Daniel M. Ginosar, Harry W. Rollins, and Robert V. Fox

SUMMARY

The EM mission faces many technical challenges involving the need to separate chemical species from one another. The need for advanced separations science includes remediation of contaminated materials in tanks and in the ground. Supercritical fluid separation is one of the possible approaches, but the science of the interface between solid (e.g., porous solids such as soil) and supercritical fluid is inadequately understood, thus limiting the potential that supercritical fluid separation has to offer for EM solutions. These fluids are held at high pressures and low temperatures and exhibit characteristics of both a liquid and a gas. Because of this, supercritical fluids have unique properties that can influence chemical reactions, extractions, and other processes in unusual ways. By gaining a better understanding of those unique properties, this task will improve supercritical fluid-based environmental remediation technologies.

This research is a fundamental investigation of the properties of a supercritical fluid at the solid-supercritical interface. It employs spectroscopic probe molecules having known photophysical mechanisms sensitive to local solvent environment effects. During FY 2000, we impregnated selected polymer thin films, having either hydrophilic or hydrophobic properties, with well characterized spectroscopic probe molecules and then determined the spectral characteristics of the probe molecules as we exposed the doped polymers to normal liquid solvents and supercritical fluids. From the data, we are developing fundamental understanding of the structure and nature of the supercritical fluid at the solid-supercritical fluid interface. The information gained from this study will improve supercritical fluid-based environmental remediation technologies. The work does not duplicate previous EM-funded work involving water as the supercritical fluid.

TASK DESCRIPTION

Matter existing in the supercritical fluid phase has been known since the early 1800s. Scientific investigation of the properties of supercritical fluids occurred in the mid-1800s, and by the late 1800s the solvent properties of supercritical fluid carbon dioxide had been reported.¹ The first large-scale commercial industrial application of supercritical fluid processing had occurred by 1936 (see Reference 1). Today, fluids in the supercritical and near-critical region, hereafter referred to collectively as critical fluids, are exploited in a number of industrial sectors, including the food and beverage, petroleum, pharmaceutical, microelectronics, and chemical industries, just to name a few. A renewed interest in critical fluids resulted during the 1970s when the U.S. faced an energy crisis and needed to become more energy efficient, and when enforcement of Federal environmental regulations brought such words as *pollution prevention* and *environmentally benign solvent* into the public arena. Recent advances in critical fluid technology have led to new applications in the areas of supercritical fluid chromatography; synthesis of aerogel and nanoparticle materials; heterogeneous catalysis; extractions of organics, metals, and radionuclides; advanced energy efficient separations; and ultrahigh-purity cleaning applications. The number of critical fluid applications has increased, owing to the unique fluid properties that can influence

chemical reactions, solubility, and material structure properties in unusual ways. The most important properties of critical fluids are (a) liquid-like solvent powers with gas-like transport properties and (b) the microscopically inhomogeneous nature of the fluid (clustering), which is much more pronounced than in liquids or gases.²⁻⁶

A significant number of fundamental investigations have been conducted during the past 20 years to understand the physical and chemical properties occurring in homogeneous, bulk critical fluids. More recently, a small number of studies focusing on the properties of critical fluid molecules adsorbed to heterogeneous solid surfaces have been conducted in the field of chromatography and for studying the physisorption of hydrogen, methane, and carbon dioxide on heterogeneous surfaces in connection with secondary energy storage technologies and carbon dioxide sequestration technologies.⁷⁻¹³ Those investigations have successfully extended existing theory describing adsorption processes of critical fluid hydrogen and methane onto heterogeneous solids, and classical adsorption isotherms have been successfully modified to fit the empirical data. Complimenting studies have been conducted by Afrane and Chimowitz for calculating and predicting thermodynamic properties of adsorbed critical fluid carbon dioxide and ethane onto solid heterogeneous surfaces.¹⁴ They caution that future investigators could arrive at erroneous conclusions if they rely too heavily on existing methods for predicting thermodynamic properties of other systems that are based on a limited number of select data available for solid/critical fluid carbon dioxide-ethane systems. Despite some initial successes focused on macroscopic solvent adsorption/desorption phenomena, a number of contradictions have arisen from experimental evidence, computer simulations, and theoretical calculations focused on macroscopic interactions at the solid/fluid interface.¹⁵⁻¹⁸ For example, Yang and Saunders speculate that, for a combination of reasons, surface clustering and multilayer formation under supercritical fluid conditions is unlikely.¹⁹ Takeba et al. have shown by way of molecular dynamics computer simulation that solvent clusters may indeed form and arrange themselves around adsorbate molecules on a MgO(001) surface.²⁰ Other investigations show evidence that adsorbate molecules are desorbed from the surface under critical fluid conditions at a bulk fluid density well below the critical point, suggesting either an extension of bulk phase properties onto the surface or direct surface clustering behavior that leads to enhanced desorption of adsorbate into the bulk fluid phase.^{9,15} The same phenomenon does not occur for adsorbate molecules under liquid or gas conditions.

These preliminary investigations point to phenomena occurring at the solid/fluid interface that, at this point, are not clearly discernable from an intrinsic property of the bulk fluid phase itself or from the surface adsorbed species. Apart from those macroscopic studies, no published experimental study to date seeks to describe phenomena occurring at the solid/fluid interface at a molecular level under critical fluid conditions. Until accurate experimental data are obtained, a molecular level description of the adsorbed phase and the adjacent fluid phase will remain unknown, the controversy will continue, predictive tools will be imprecise, and our understanding will not be advanced. We will fail to exploit the fluid properties of critical fluids and lag behind in design and development of new critical fluid techniques useful for solving EM-50 problems.

This research will directly address EM-50 problems by promising better understanding of chemical reaction and mass transport phenomena occurring at the solid/fluid interface. Liquid solvent and critical fluid solvent extraction techniques hold very high potential for selectively extracting hazardous and recalcitrant compounds from liquid and solid environmental media. The research focuses on the molecular level chemical and physical phenomena occurring at the solid/fluid interface. Research for FY 2000 involved initiation of an innovative exploration of the fundamental properties of fluids at the solid/fluid interface. The goal was to obtain quantitative information regarding the structure of a supercritical fluid at the solid/supercritical fluid interface as a function of fluid density using well known and well understood spectroscopic probe molecules. The research was broken into three subtasks: (a) spectroscopic probe molecule selection and characterization, (b) polymer selection and

characterization, and (c) characterization of probe-doped-polymers in carbon dioxide. Each subtask, with its associated milestone, is described below.

1. *Spectroscopic probe molecule selection and characterization.* We selected and screened fluorescent probe molecules with known photophysical mechanisms for spectral responsiveness in solvents having different polarity. The desired trait is for either the shape of the spectral band to change as a function of solvent polarity or the wavelength of maximum absorbance to shift as a result of changes in solvent polarity, or both. Two dye molecules were selected and investigated in FY 2000.
2. *Polymer selection and characterization.* We selected and further characterized polymers having either hydrophobic or hydrophilic properties and capable of being cast into thin films. Characterization included a study of solubility, swelling, and chemical compatibility with carbon dioxide. Characterization also included a study of the probes' spectral response in the presence of the polymer. We entrained probe molecules into a polymer and cast the mixture into a thin film on a quartz slide. Two polymers were investigated in FY 2000.
3. *Characterization of probe-doped-polymers in carbon dioxide.* We made probe-doped-polymers, cast them into thin films, then subjected them to liquid, gas, and supercritical fluid carbon dioxide conditions. We determined the spectral response of the probes in carbon dioxide and other solvents as a function of solvent condition, and we determined the spectral response of probes in the polymer thin films. The results from this characterization are the basis of a comparative study.

ACCOMPLISHMENTS

Optical cells were designed for use at pressures up to 5,000 psi and temperatures up to 100°C. Additional high-pressure optical cells for fluorescence and absorption measurements were designed and manufactured based on the Clemson design.

The absorption spectral properties of the probe molecule, Nile red, were evaluated in a series of liquid organic solvents (Figure 1). As the solvent polarity changed from hexane to methanol, we observed both a change in the shape of the peak and a shift toward the red. Nile red exhibits excellent properties as a probe of solvent polarity in this regard. A plot of the absorption peak width as a function of solvent polarity (E_t^N) demonstrates a relatively linear response for this probe molecule (see Figure 2).

We also completed a more extensive investigation of the fluorescence spectral properties of the probe molecule Nile red in organic solvents (see Figure 3). The fluorescence response exhibits a spectral shift, a change in the shape of the emission band, and a change in relative fluorescence quantum yield. This type of spectral response exhibited by Nile red is an excellent example of an ideal probe. A plot of the fluorescence peak maximum versus solvent polarity also yields a relatively linear probe response (see Figure 4).

The solubility and spectral properties (absorbance and fluorescence) of Nile red in supercritical carbon dioxide at 35°C were determined as a function of pressure (Figures 5, 6, and 7). Figure 5 demonstrates the solubility of Nile red in carbon dioxide as a function of pressure and provides the characteristics of the absorption band in carbon dioxide solvent. A plot of absorbance versus pressure shows the pressure dependence of solubility for Nile red (Figure 6). The fluorescence spectra of Nile red in carbon dioxide exhibits a change in the shape of the emission peak and a spectral shift toward shorter wavelengths (blue) as the pressure of the carbon dioxide solvent is increased (Figure 7). The probe's response in carbon dioxide is to be compared and contrasted with the response of the probe toward liquid solvents.

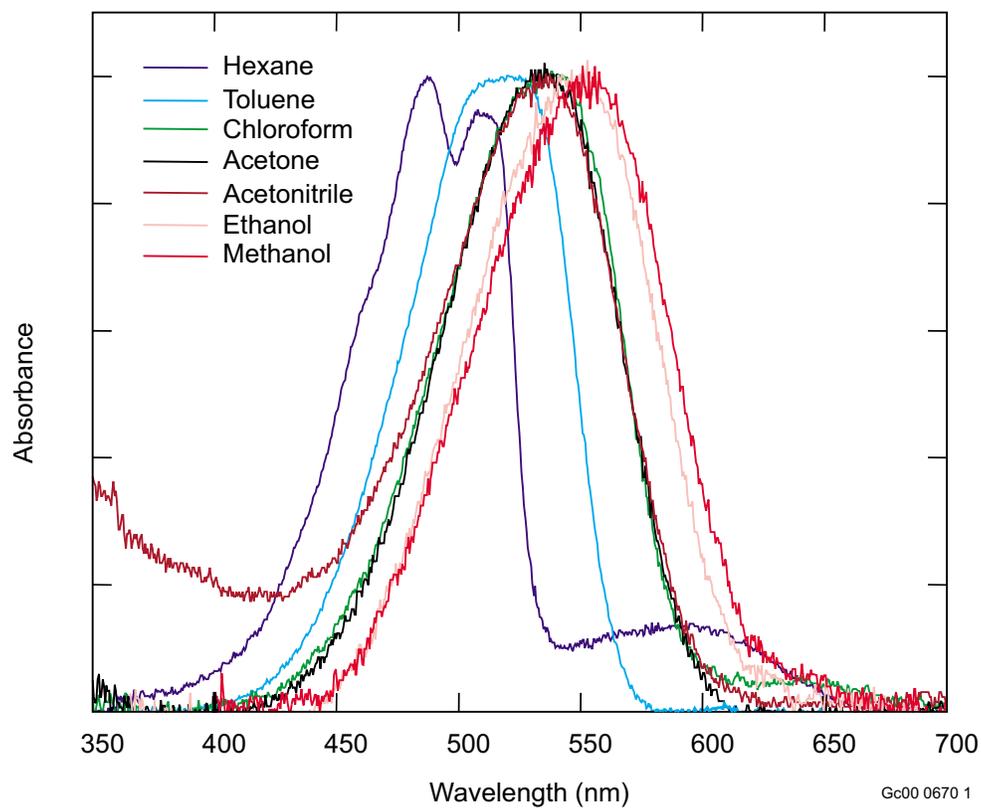


Figure 1. Absorbance Spectra of Nile red in various solvents.

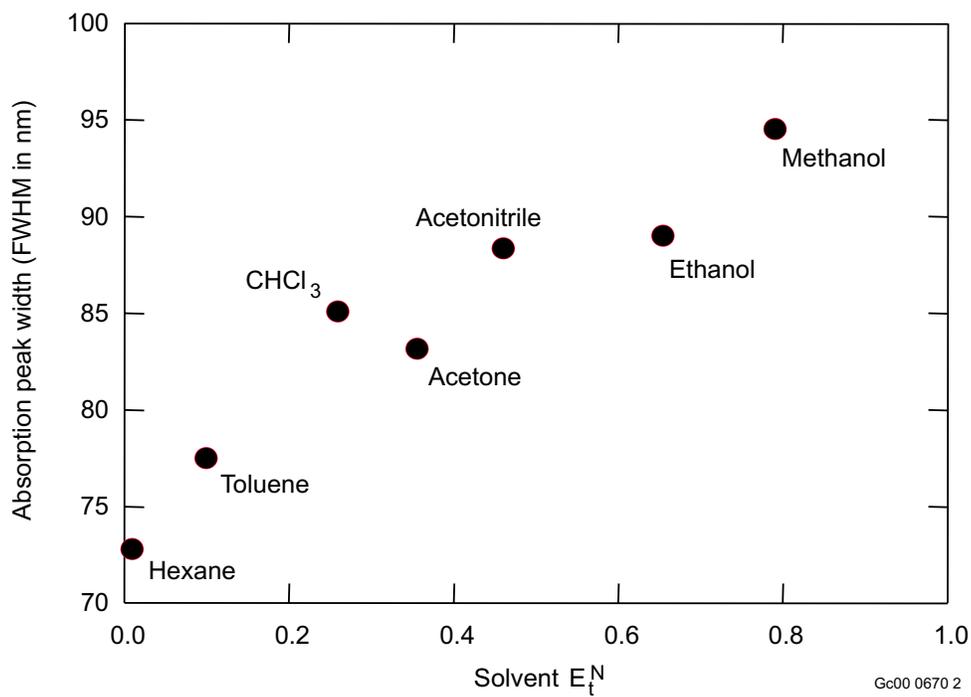


Figure 2. Plot of Nile red absorbance peak FWHM in various liquid solvents

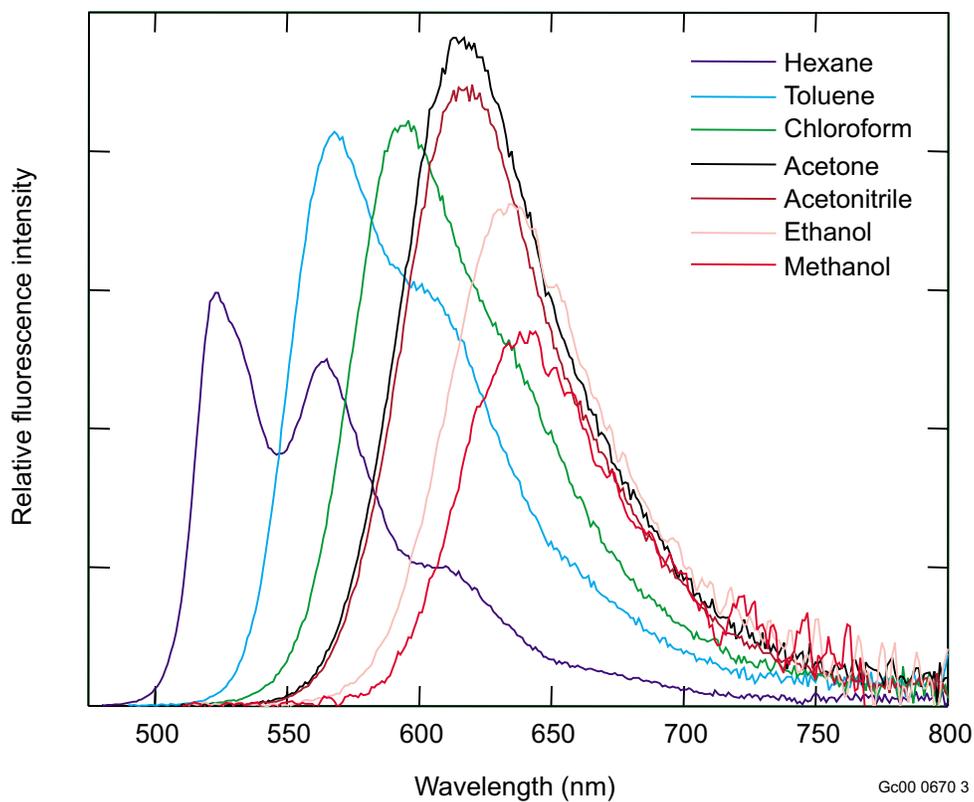


Figure 3. Florescent spectra of Nile red in various liquid solvents.

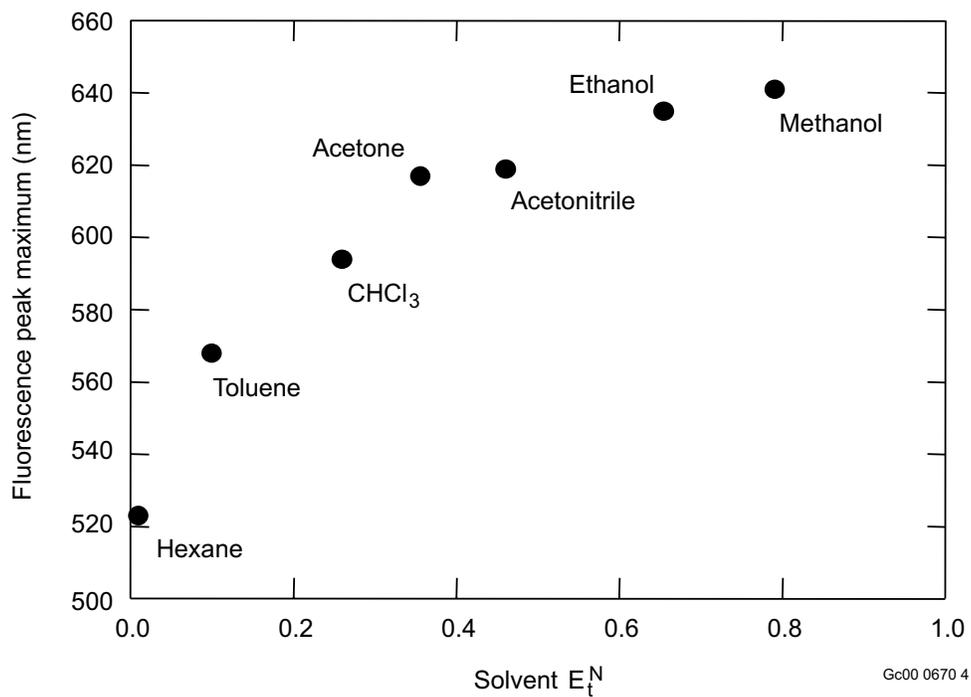


Figure 4. Plot of florescent peak max of Nile red in various liquid solvents.

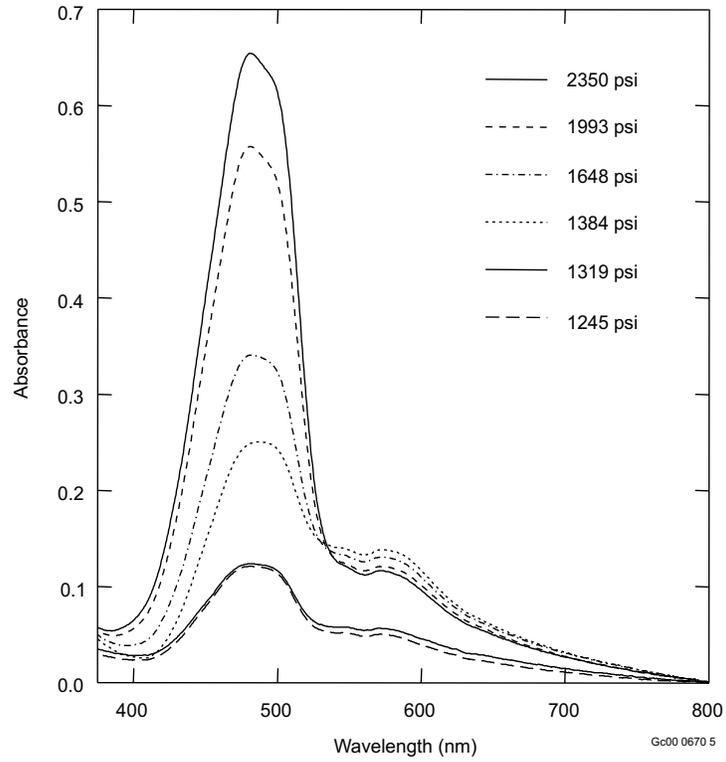


Figure 5. Nile red in CO₂ at 35°C.

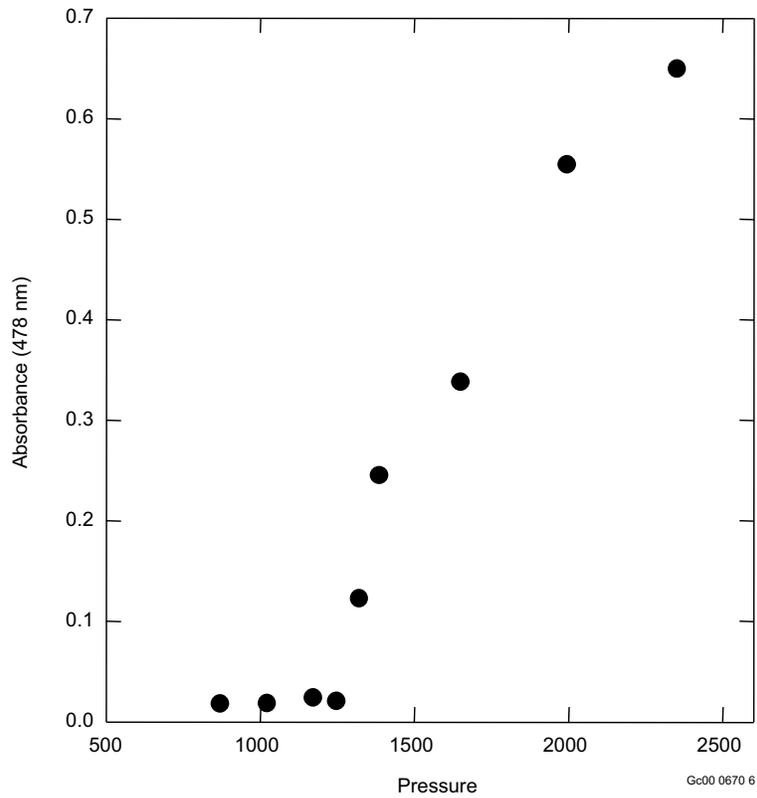


Figure 6. Nile red in CO₂ at 35°C.

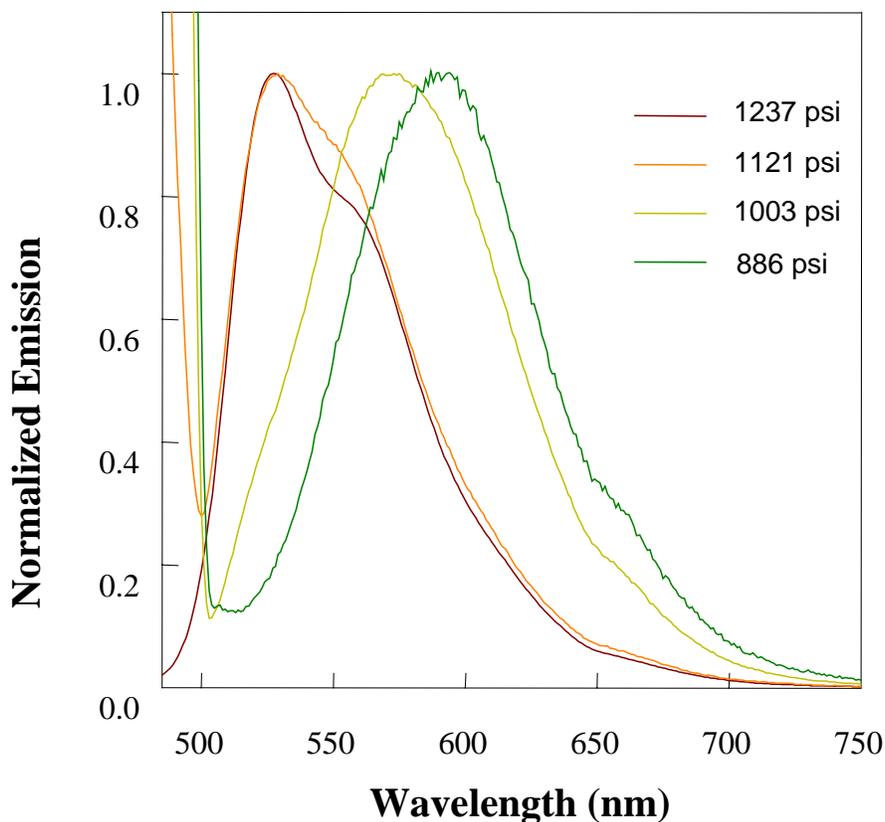


Figure 7. Fluorescence spectra of Nile red in CO₂ at 35°C.

We prepared and doped thin films of the polymer poly(methyl methacrylate) (PMMA) with Nile red. Thin PMMA films containing Nile red were soaked in hexane, toluene, and methanol, and the fluorescence spectra were monitored as a function of time. The PMMA/Nile red film soaked in hexane showed very little change, even after soaking for four days due to poor swelling of the PMMA film by hexane. The PMMA/Nile red soaked in toluene showed a systematic shift with time; however, the shift was relatively minor due to the similarity of the Nile red fluorescence spectra in toluene and in PMMA films. The fluorescence peak maximum for PMMA/Nile red films soaked in methanol shift from 575 nm in PMMA to 612 nm after soaking in methanol for 95 minutes and is the most notable example of spectral shift of the probe in the polymer (see Figure 8). The large spectral shift is due to both the high degree of swelling of the polymer by methanol and the large difference in the Nile red spectra in methanol and in PMMA films. Figure 9 shows the fluorescence spectra of PMMA/Nile red films in the presence of supercritical CO₂. The same figure shows that in the presence of CO₂, the observed spectra shows a large shift and a decrease in intensity. The decrease in intensity is due to the extraction of the Nile red from the PMMA film. Current investigations are focusing on the dynamics of PMMA swelling in CO₂ and quantitating the degree of extraction of Nile red. It is likely that if significant amounts of Nile red leach from the polymer, then the polymer/Nile red spectra will be indistinguishable from the carbon dioxide phase Nile red, thus rendering the probe useless for evaluation.

We have initiated studies using Nile red in polystyrene and ethidium bromide, Reichardt's dye, and Nile blue A in PMMA. We chose these systems in an attempt to limit the extraction of the dye into the solvent. Results are pending. A draft publication on the two dyes and two polymers we were able to study in FY 2000 is targeted for Fall 2000.

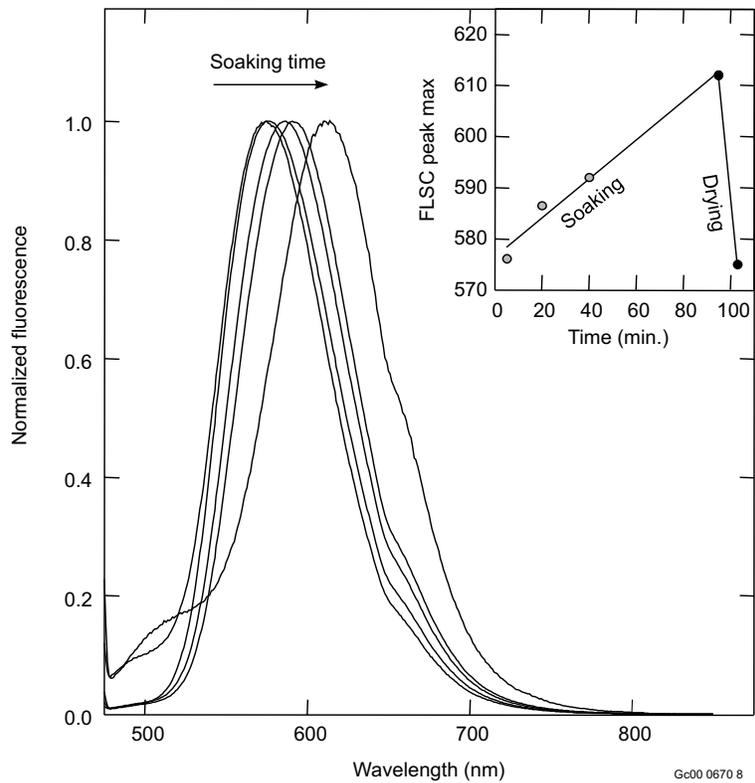


Figure 8. Nile red in methanol-swollen PMMA films.

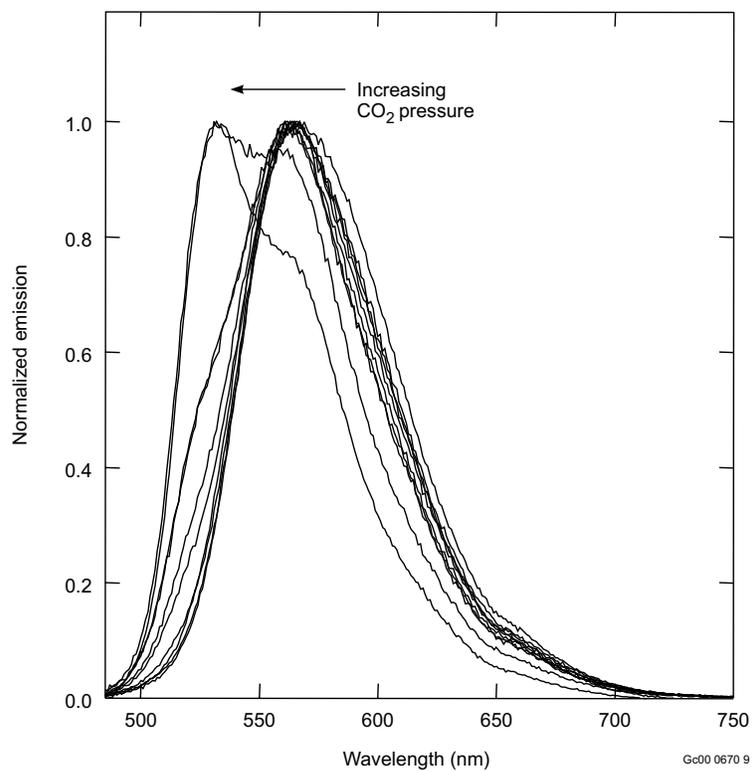


Figure 9. Nile red in CO₂-swollen PMMA at 35°C.

REFERENCES

1. M. McHugh and V. Krukonis, *Supercritical Fluid Extraction*, 2nd Edition, Butterworth–Heinemann Publishers, Boston, MA., 1994.
2. S. Kim and K. P. Johnston, *AIChE J.*, 1987, 33, 1603.
3. S. Kim and K. P. Johnston, *Ind. Eng. Chem. Res.*, 1987, 26, 1206.
4. P. G. Debenedetti, *Chem. Eng. Sci.*, 1987, 42, 2203.
5. Y. P. Sun et al., *Chem. Phys. Lett.*, 1993, 210, 111.
6. Y. P. Sun, et al., *Ber. Bunsenges. Phys. Chem.*, 1995, 99, 976.
7. C. R. Clarkson, et al., *Carbon*, 1997, 35(12), 1689–1705.
8. P. Braeuer, et al., *Separation and Purification Technology*, 1997, 12, 255–263.
9. T. Nitta and T. Shigeta, *Fluid Phase Equilibria*, 1998, 144, 245–256.
10. A. Shapiro and S. Erling, *Fluid Phase Equilibria*, 1999, 158–160, 565–573.
11. L. Zhou, and Y. Zhou, *Chemical Engineering Science*, 1998, 53(14), 2531–2536.
12. G. L. Aranovich, and M. D. Donohue, *Carbon*, 1995, 33(10), 1369–1375.
13. K. Kaczmarek and D. Antos, *Journal of Chromatography A*, 1999, 862, 1–16.
14. G. Afrane and E. H. Chimowitz, *Fluid Phase Equilibria*, 1995, 111, 213–238.
15. K. Murata and K. Kaneka, *Chemical Physics Letters*, 2000, 321, 342–348.
16. L. L. Lee and H. D. Cochran, *Journal of Supercritical Fluids*, 1998, 13, 77–81.
17. C. Tapia–Corzo, et al., *Journal of Supercritical Fluids*, 2000, 17, 25–33.
18. G. M. Martinez and D. Basmadjian, *Chemical Engineering Science*, 1996, 51(7), 1043–1054.
19. R. T. Yang and J. T. Saunders, *Fuel*, 1985, 64, 616.
20. H. Takeba, et al, *Surface Science*, 1996, 357–358, 703–707.

Appendix A
Publications and Presentations

Publications and Presentations

Publications

Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship

G. A. Cordes, "Patterns and Intelligent Systems," *Nuclear Technology*, submitted July 2000.

Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-Term Stewardship Concerns and Development of Improved Modeling Methods

M. L. Abbott, D. D. Susong, D. P. Krabbenhoft, "Mercury Deposition in Snow Near an Industrial Emission Source in Southeastern Idaho and the Teton Range, Wyoming," Kluwer Academic Publishers, *Water, Air, and Soil Pollution*, July 11, 2000.

Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface

L. D. Cecil, J. A. Welhan, E. R. Sudicky, and J. R. Green, "Use of Chlorine-36 to Determine Regional-Scale Aquifer Dispersivity, Snake River Plain Aquifer, Idaho/USA," *Nuclear Instruments and Methods in Physics Research*, B 172, pp. 679–687, 2000.

L. D. Cecil, L. L. Knobel, J. R. Green, and S. K. Frape, "In Situ Production of Chlorine-36 in the Eastern Snake River Plain Aquifer, Idaho: Implication for Describing Ground-Water Contamination Near a Nuclear Facility," *U.S. Geological Survey Water Resources Investigations Report*, 00-4114, 2000.

L. D. Cecil and J. R. Green, "Radon-222 as a Tracer in the Hydrogeologic Environment," *Environmental Tracers in Subsurface Hydrology*, eds., P. G. Cook, and A. L. Herczeg, Kluwer Academic Publishers, pp. 175–194, 2000.

L. D. Cecil, J. R. Green, and D. L. Naftz, "Global Ice-Core Research: Understanding and Applying Environmental Records of the Past," *U.S. Geological Survey Fact Sheet*, FS-003-00, 2000.

S. N. Davis, L. D. Cecil, M. Zareda, and S. Moysey, "Chlorine-36, Bromide, and the Origin of Spring Water," in press for a special issue, *Journal Chemical Geology*.

J. R. Green, L. D. Cecil, D. L. Naftz, H. A. Sinal, K. J. Kreutz, V. B. Aizen, C. P. Wake, and S. K. Frape, "Cosmogenic Isotopes in Mid-latitude Glacial Environments in the Northern Hemisphere, Indicators of Global Fallout," *Nuclear Instruments and Methods in Physics Research*, B 172, pp. 812–816, 2000.

T. M. Johnson, R. C. Roback, T. L. McLing, T. D. Bullen, D. J. DePaolo, C. Doughter, R. J. Hunt, R. W. Smith, L. D. Cecil, and M. T. Murrell, "Groundwater 'Fast Paths' in the Snake River Plain Aquifer: Radiogenic Isotope Ratios as Natural Groundwater Tracers," *Geology*, 2000.

R. H. Morin, G. E. Descamps, and L. D. Cecil, "Characterizing Englacial Structure from Analysis of Acoustic Televiwer Logs, Upper Fremont Glacier, Wyoming," *Proceedings of the Seventh*

International Symposium on Geophysics for Minerals, Geotechnical, and Groundwater Applications, October 24–26, pp. 235–243, 2000,

R. H. Morin, G. E. Descamps, and L. D. Cecil, “Acoustic Televiewer Logging in Glacier Boreholes, in press, *Journal of Glaciology*, Vol. 46, No. 15.

Geological, Geophysical, and Hydrological Environs of the INEEL Site

G. F. Embree, “Geologic Map of the Moody 7.5 Minute Quadrangle, Eastern Idaho; Idaho Geological Survey Map,” in review, 2000.

G. F. Embree, “Geologic Map of the White Owl Butte 7.5 Minute Quadrangle, Eastern Idaho; Idaho Geological Survey Map,” in review, 2000.

G. F. Embree, “Geologic Map of the Wright Creek 7.5 Minute Quadrangle, Eastern Idaho; Idaho Geological Survey Map,” in review, 2000.

Complex Systems Theory Applied to Subsurface Transport

B. A. Faybishenko, P. A. Witherspoon, C. Doughty, T. R. Wood, R. K. Podgorney, and J. T. Geller, “Multiscale Investigations of Liquid Flow in the Vadose Zone of Fractured Basalt,” *Geophysical Monograph*, “*Flow and Transport in Fractured Rocks*,” *American Geophysical Union*, T. Nicholson ed., In Review.

B. A. Faybishenko, C. Doughty, M. Steiger, J. C. S. Long, T. R. Wood, J. Jacobsen, J. Lore and P. Zawislanski, “Conceptual Model of the Geometry and Physics of Fluid Flow and Chemical Transport in Unsaturated Fractured Basalt: Box Canyon Site, Idaho,” *Water Resources Research*, 37(12), pp. 3499–3522, 2000.

R. K. Podgorney, T. R. Wood, B. A. Faybishenko, and T. M. Stoops, “Unstable Infiltration Into Variably Saturated Fractured Basalt On a 1-Meter Field Scale,” in *Geophysical Monograph “Dynamics of Fluids in Fractured Rocks: Concepts and Recent Advances,” American Geophysical Union*, 2000.

T. R. Wood, R. K. Podgorney, and B. Faybishenko, Small-Scale Field Tests of Water Flow In a Fractured Rock Vadose Zone, Case Study to Chapter 3 of the book “*Vadose Zone Science and Technology Solutions*,” B. Looney and R. Falta, eds., Battelle Press, OH, 2000.

Environmental Separations and Barriers

G. B. Cotton and H. B. Eldridge, “Nanolevel Magnetic Separation Model Considering Flow Limitations,” *Chemical Engineering Science*, submitted May 2000, accepted June 2000.

G. B. Cotton, “Magnetic Separations With Magnetite: Theory, Operation and Limitations,” Ph. D. Dissertation, University of Idaho, 2000.

Presentations

Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-term Stewardship Concerns and Development of Improved Modeling Methods

M. L. Abbott, D. D. Susong, D. P. Krabbenhoft, "Comparison of Mercury Measurements in Snow with ISCST3 Model-Predicted Deposition Near an Industrial Emission Source in Southeastern Idaho," presented at the *International Symposium on the Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, September 12–14, 2000* (proceedings in press).

M. L. Abbott, D. D. Susong, D. P. Krabbenhoft, M. L. Olson, "Mercury Distribution in Soil Near a Major Atmospheric Emission Source at the Idaho National Engineering and Environmental Laboratory in Southeastern Idaho," <http://www.geosociety.org/pubs/abstracts/2000/50248.htm>, *Geological Society of America (Summit 2000) Annual Meeting, Reno, NV, November 9–18, 2000*.

D. D. Susong, M. L. Abbott, D. P. Krabbenhoft, "Mercury Accumulation in Snow on the Idaho National Engineering and Environmental Laboratory and Surrounding Region, Southeastern Idaho," <http://www.geosociety.org/pubs/abstracts/2000/50087.htm>, *Geological Society of America (Summit 2000) Annual Meeting, Reno, NV, November 9–18, 2000*.

Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes

J. C. Ingram, F. S. Colwell, R. M. Lehman, W. F. Bauer, A. Shaw, "Secondary Ion Mass Spectrometry Investigation of Interfacial Chemistry of Intact Microorganisms," *American Geophysical Union, San Francisco, CA, December 2000*.

J. C. Ingram, F. S. Colwell, R. M. Lehman, W. F. Bauer, A. Shaw, "Interrogation of Intact Microorganisms by Static Secondary Ion Mass Spectrometry," *47th American Society for Mass Spectrometry Meeting in Long Beach, CA, June 2000*.

J. C. Ingram, F. S. Colwell, R. M. Lehman, W. F. Bauer, A. Shaw, "Static Secondary Ion Mass Spectrometry Analysis of Intact Microorganisms," *Joint 55th NORM/16th Rocky Mountain Regional ACS Meeting, Idaho Falls, ID, June 2000*.

Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface

J. R. Green, L. D. Cecil, and D. L. Naftz, "USGS Research on Three Mid-Latitude Glaciers," *Western Snow Conference, Port Angeles Washington, April 2000*.

L. D. Cecil, J. R. Green, D. L. Naftz, P. F. Schuster, D. D. Susong, "The U.S. Geological Survey's Global Ice Core Research Program," *Lanzhou Institute of Glaciology, Chinese Academy of Sciences, April 2000*.

L. DeWayne Cecil, Jaromy R. Green, David L. Naftz, Paul F. Schuster, David D. Susong, "The U.S. Geological Survey's Global Ice Core Research Program," *National Polar Research Institute, University of Tokyo, Japan, April 2000*.

L. D. Cecil and J. R. Green, "Global Environmental Change Research: Evidence in Mid-Latitude Glaciers," *Idaho State University Lecture Series*.

Complex Systems Theory Applied to Subsurface Transport

T. R. Wood, D. Stoner, C. Tolle, J. James, D. Peak, B. Faybishenko, and J. Crepeau, "Can a Fractured Basalt Vadose Zone be characterized as a Complex System?," *Summit 2000, Abstracts with Programs, Volume 32, Number 7, Geological Society of America, Annual Meeting and Exposition, November 9–18, 2000, Reno, Nevada, 2000*.

Unified Hydrogeophysical Parameter Estimation Approach Subsurface Contaminant Transport—Subsurface Imaging Collaboration With the Center for Subsurface Sensing and Imaging Systems

E. D. Mattson, "Underground Pollution Assessment," *CenSSIS Retreat, Center for Subsurface Sensing and Imaging Systems, Woods Hole Oceanographic Institution, Quisset Campus, June 4–6, 2000*.

Environmental Separations and Barriers

L. A. Polson, M. L. Stone, and G. L. Gresham, "Characterization of Phosphazene Materials as Membranes in Membrane Introduction Mass Spectrometry (MIMS)," Poster (070), *2000 Northwest and Rocky Mountain Joint Regional Meeting, Idaho Falls, ID, June 15–17, 2000*.

M. L. Stone, L. A. Polson, and G. L. Gresham, "Analysis of Chlorocarbon Transport Through Polymeric Membranes Using Membrane Introduction Mass Spectrometry," Oral Presentation (096), *2000 Northwest and Rocky Mountain Joint Regional Meeting, Idaho Falls, ID, June 15–17, 2000*.

Linda Polson, Mark Stone, and Gary Gresham, "Membrane Introduction Mass Spectroscopy (MIMS): An Overview of System Components and Variables," *National American Chemical Society Meeting, Washington, D.C., August 22, 2000*.

Appendix B

**Comparison of ESRC Tasks with EM
Site Technology Coordination Group Needs**

Comparison of ESRC Tasks with EM Site Technology Coordination Group Needs

This appendix summaries how ESRC tasks link with EM needs as captured in the Site Technology Coordination Group (STCG) database. This summary was created for two reasons:

- To help ensure that ESRC funds were being used to address EM needs.
- To formulate a methodology for integrating research and development efforts at the INEEL with Site Operations, thereby facilitating moving science and technology toward ultimate demonstration and deployment.

ESRC and the INEEL Integration and Roadmapping (II&R) Department linked ESRC tasks to EM Site Operational Needs. Those needs, which are tabulated in the STCG, were mapped to the research in each of the funded tasks. II&R maintains the STCG database.

The ESRC tasks are tabulated and mapped to STCG needs (see Table B-1). All research activities had a link to one or more identified site needs.

The planned application of this approach in FY 2001 to other R&D programs will improve the process of moving science and technology toward real EM needs.

This mapping is facilitating improving communication between R&D and Operational Users, e.g., arranging selected meetings between Pis and STCG end users. Finally, a series of ESRC seminars were established to disseminate information on the progress of the research effort and to provide focus and feed back from operational personnel.

Table B-1. ESRC tasks tabulated and mapped to STCG needs.

Task Title	STCG ID No.	STCG Description
Nondestructive Assay (NDA) Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship	1.1.09	Nondestructive Radiological Assay Methods for SNF
	3.1.06	Advanced Nuclear Assay for CH-TRU Waste Drums
	3.1.32	Develop Nondestructive Assay (NDA) Capability for Remote-Handled TRU Waste and Contact-Handled TRU Waste with Shielded RH Components
	3.1.42	Non Destructive Assay for RCRA metals and chlorine in WERF incinerator feed
	3.1.46	Develop Nondestructive Examination (NDE) Capability for Remote-Handled TRU Waste and Contact-Handled TRU Waste with Shielded RH Components
	S.1.05	Nondestructive Assay (NDA) Capability for Remote-Handled Transuranic Waste
Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-term Stewardship Concerns and Development of Improved Modeling Methods	2.1.36	Mercury Removal from Liquid Wastes
	2.1.56	Mercury Treatment for Aluminum Calcine
	3.1.49	Mercury Emissions Control for Mixed Waste Thermal Treatment
Ion Mobility Spectrometry for Environmental Monitoring and In Situ Measurements of Hazardous Organics	2.1.18	Continuous Emissions Monitor for Offgas Analysis
	2.1.19	EPA Methods Sample Collection and Analysis Verification/Development
	6.1.02	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
	6.1.27	Integrated Suite of In Situ Instruments to Determine Flux in the Vadose Zone
	6.1.30	Instrumentation to Reliably Measure Soil Gas Flux Accounting for Barometric and Temporal Variations
	7.2.17	Field Screening of Samples and Equipment Surfaces to Identify PCB Contamination
	S.1.01	Microbial Alteration of Heavy Metal and Radionuclide Partitioning at Mineral Surfaces
Molecular Engineering and Genomics For Development of Environmental Biosensors Using Robust Biocatalysts	S.1.06	Detect and Mitigate Microbiologically Induced Corrosion in Spent Nuclear Fuel Dry Storage Containers

Table B-1. Continued.

Task Title	STCG ID No.	STCG Description
	S.1.19	In Situ Biologic Activity Sensor for Vadose Zone and Groundwater Monitoring, Characterization and Remediation
Biologically Based Catalysts as Sensors to Detect Contaminants in Harsh Service Environment	6.1.02	Real-time Field Instrumentation for Characterization Monitoring Soils and Groundwater
	S.1.04	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
	S.1.19	In Situ Biologic Activity Sensor for Vadose Zone and Groundwater Monitoring, Characterization and Remediation
Determining Soil Moisture Over Wide Areas for DOE Site Stewardship Hydrology	6.1.02	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
Advanced Robotic Technologies for Remote Environmental Surveillance and Stewardship	2.1.26	Direct Tank Sampler for Tank Solution Characterization
	3.1.46	Develop Nondestructive Examination (NDE) Capability for Remote-Handled TRU Waste and Contact-Handled TRU Waste with Shielded RH Components
	7.2.06	Remote Characterization for Building Release, Large Area Surface Soil Characterization, and Characterization of Sumps, Debris, Underwater Areas, and Buried Pipes and Utilities
	7.2.08	Robotics for D&D
	7.2.19	Remote/Robotic Technologies for Access and Deployment of Characterization and Sampling Tools
Isobaric Groundwater Well for Precise Water Level Measurement Relevant to Long Term Surveillance and Stewardship	6.1.02	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
	6.1.04	In-situ Treatment of VOC Contaminated Groundwater in Saturated and Unsaturated Deep Fractured Rock
	S.1.04	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
	S.1.11	Modeling of Flow and Transport in the Vadose Zone
	S.1.17	Development of Sensors for Large Scale Measurements in the Vadose Zone to Define Spatial Variability

Table B-1. Continued.

Task Title	STCG ID No.	STCG Description
Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes	6.1.25	Pretreatment of Explosives Contaminated Soil for Biological Remediation
	S.1.01	Microbial Alteration of Heavy Metal and Radionuclide Partitioning at Mineral Surfaces
Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface	S.1.16	Quantifying Uncertainty in Risk Calculations
Geological, Geophysical and Hydrological Environs of the INEEL Site	S.1.10	Geochemistry of Contaminants in the Vadose Zone
	S.1.11	Modeling of Flow and Transport in the Vadose Zone
	S.1.19	In Situ Biologic Activity Sensor for Vadose Zone and Groundwater Monitoring, Characterization and Remediation
Complex Systems Theory Applied To Subsurface Transport	S.1.09	Characterization of Scale and Spatial Heterogeneity and Preferential Flow
	S.1.10	Geochemistry of Contaminants in the Vadose Zone
	S.1.11	Modeling of Flow and Transport in the Vadose Zone
	S.1.12	Understanding the Behavior of Waste Forms and their Near-Field Transport
	S.1.15	Physics of Flow in the Vadose Zone
	S.1.17	Development of Sensors for Large Scale Measurements in the Vadose Zone to Define Spatial Variability
	6.1.24	Understanding the Migration of VOCs Around an ISV Melt
Ecological Engineering of Rhizosphere Systems	6.1.32	In Situ Stabilization Techniques to Isolate Metals and Radionuclides from the Biosphere, including both Surface and Deep Fractured Rock
	2.1.17	Develop New Filter Leach Process
	3.1.33	Develop In-Situ Hydrogen and Volatile Organic Compound (VOC) Reduction
	7.2.09	Develop a Rapid Wood Radiological Contamination Monitor
Investigation of Factors Influencing Cesium Mobility and Uptake in Plant/Soil Systems	S.1.12	Understanding the Behavior of Waste Forms and their Near-Field Transport
	2.1.28	Cs and Sr Removal from Newly Generated Liquid Waste
Long-term Biogeochemical Destruction and Control of Aquifer Contaminants Using Single-Well Push-Pull Tests	6.1.32	In Situ Stabilization Techniques to Isolate Metals and Radionuclides from the Biosphere, including both Surface and Deep Fractured Rock

Table B-1. Continued.

Task Title	STCG ID No.	STCG Description
Unified Hydrogeophysical Parameter Estimation Approach to Subsurface Contaminant Transport—Subsurface Imaging Collaboration With the Center for Subsurface Sensing and Imaging Systems	S.1.09	Characterization of Scale and Spatial Heterogeneity and Preferential Flow
	S.1.17	Development of Sensors for Large Scale Measurements in the Vadose Zone to Define Spatial Variability
	S.1.18	Development of Indirect Sensing Instrumentation for Spatial Variability Analyses of State Variables
Innovative Approaches to Characterize Vadose Zone Hydraulics Properties	S.1.09	Characterization of Scale and Spatial Heterogeneity and Preferential Flow
	S.1.10	Geochemistry of Contaminants in the Vadose Zone
	S.1.11	Modeling of Flow and Transport in the Vadose Zone
	S.1.17	Development of Sensors for Large Scale Measurements in the Vadose Zone to Define Spatial Variability
	S.1.19	In Situ Biologic Activity Sensor for Vadose Zone and Groundwater Monitoring, Characterization and Remediation
	6.1.02	Real-time Field Instrumentation for Characterization and Monitoring Soils and Groundwater
	6.1.04	In-situ Treatment of VOC Contaminated Groundwater in Saturated and Unsaturated Deep Fractured Rock
Computing Framework for Environmental Cleanup, Restoration, and Long-term Stewardship	6.1.27	Integrated Suite of In Situ Instruments to Determine Flux in the Vadose Zone
	S.1.11	Modeling of Flow and Transport in the Vadose Zone
	S.1.12	Understanding the Behavior of Waste Forms and their Near-Field Transport
	S.1.13	Longevity of Engineered Barriers
	S.1.14	Transport of Contaminants in the Vapor Phase
Decontamination, Decommissioning, and Remediation Optimal Planning System for the Advanced Decontamination and Decommissioning System	S.1.16	Quantifying Uncertainty in Risk Calculations
	7.2.21	Removal of Two Reactors as Single Units
	7.2.29	Remote Demolition of Machinery
	7.2.30	Remote Demolition of Metal Structures
	7.2.31	Remote Demolition of Piping

Table B-1. Continued.

Task Title	STCG ID No.	STCG Description
Waste Characterization and Sorting Station for the Advanced Decontamination and Decommissioning System	7.2.08	Robotics for D&D
	7.2.23	Copper Wire Recycle
	7.2.27	Reuse of Metal Pipes, Lumber, Lead, and Other Metals
Robotic Waste Packaging System for the Advanced Decontamination and Decommissioning System	7.2.08	Robotics for D&D
	7.2.23	Copper Wire Recycle
	7.2.27	Reuse of Metal Pipes, Lumber, Lead, and Other Metals
Environmental Separation and Barriers	S.1.01	Microbial Alteration of Heavy Metal and Radionuclide Partitioning at Mineral Surfaces
Proton Conducting Ceramic Membrane Applied to Spent Nuclear Fuel Stewardship	2.1.64	Solid-Liquid Separation Equipment Development and Application
	3.1.33	Develop In-Situ Hydrogen and Volatile Organic Compound (VOC) Reduction
Spectroscopic Investigations at Solid Supercritical Fluid Interfaces in Support of Advanced Supercritical Separation Techniques	2.1.06a	TRU and Sr Removal from High Activity Waste
	2.1.06b	Cs Removal from High Activity Waste
	2.1.25	Ion-Exchange System for Water Runoff
	2.1.28	Cs and Sr Removal from Newly Generated Liquid Waste
	2.1.56	Mercury Treatment for Aluminum Calcine
	2.1.66	Treatment/Disposition of Spent Ion Exchange Resins
	2.1.68	Technetium Removal from INEEL High Level Waste
	7.2.14	Technology for Decontaminating Radionuclide Contaminated Lead Shot, Brick (including lead plate), and Sheeting Allowing Free-Release
	S.2.06	Understanding the Physics and Chemistry of Metal Decontamination
	S.1.10	Geochemistry of Contaminants in the Vadose Zone
	S.2.05	Understanding the Physics and Chemistry of Concrete Decontamination

Appendix C
ESRC Portfolio Characterization

ESRC Portfolio Characterization

This appendix characterizes the ESRC portfolio from the perspectives of technology maturity and building INEEL R&D capabilities relevant to the DOE-EM mission. ESRC objectives include providing science and technology for meeting the DOE-EM mission and enhancing the INEEL's science and technology capabilities for longer-term challenges like environmental stewardship.

Technology Maturity

DOE-EM categorizes technology maturity in seven stages or "gates":

1. Basic Research
2. Applied Research
3. Exploratory Development
4. Advanced Development
5. Engineering Development
6. Demonstration
7. Deployment

We categorized the 24 tasks that started in FY 2000 according to this scheme. Figure C-1 illustrates the portfolio. Two-thirds of the work is applied research; this is fully appropriate given ESRC objectives. Also consistent with the objectives and nature of ESRC, none of the tasks were categorized at stages 5 through 7 (see Table C-1).

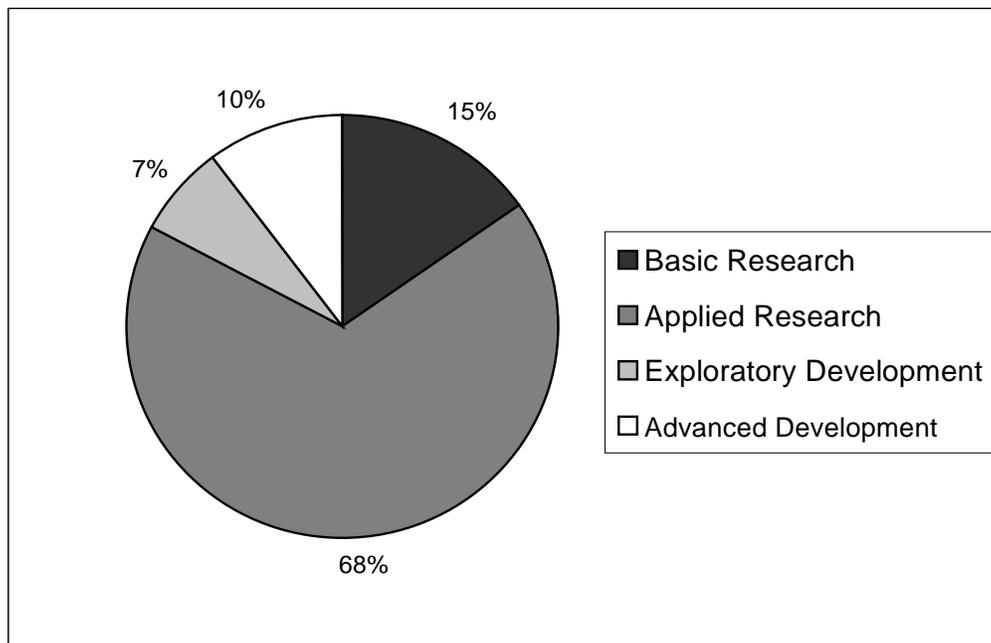


Figure C-1. ESRC portfolio funding by technology maturity.

Table C-1. Technology maturity of ESRC tasks.

Title	Technology Maturity P = Primary type; S = secondary type						
	Basic Research	Applied Research	Exploratory Development	Advanced Development	Engineering Development	Demonstration	Deployment
Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship		S	P	S			
Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-term Stewardship Concerns and Development of Improved Modeling Methods		P	S				
Ion Mobility Spectrometry for Environmental Monitoring and In Situ Measurement of Hazardous Organics		P	S				
Molecular Engineering and Genomics for Development of Environmental Biosensors Using Robust Biocatalysts	S	P					
Biologically Based Catalysts as Sensors to Detect Contaminants in Harsh Service Environments	S	P					
Determining Soil Moisture Over Wide Areas for DOE Site Stewardship Hydrology			P				
Advanced Robotic Technologies for Remote Environmental Surveillance and Stewardship	S	S	P				
Isobaric Groundwater Well for Precise Water Level Measurement Relevant to Long Term Surveillance and Stewardship		S		P			
Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes		P					
Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface	P	S					
Geological, Geophysical and Hydrological Environs of the INEEL Site	P	S	S				
Complex Systems Theory Applied to Subsurface Transport	S	P					

Table C-1. Continued.

Title	Technology Maturity P = Primary type; S = secondary type						
	Basic Research	Applied Research	Exploratory Development	Advanced Development	Engineering Development	Demonstration	Deployment
Ecological Engineering of Rhizosphere Systems	P	S					
Investigation of Factors Influencing Cesium Mobility and Uptake in Plant/Soil Systems	P	S					
Long-Term Biogeochemical Destruction and Control of Aquifer Contaminants Using Single-Well Push-Pull Tests		P					
Unified Hydrogeophysical Parameter Estimation Approach to Subsurface Contaminant Transport—Subsurface Imaging Collaboration with the Center for Subsurface Sensing and Imaging Systems		P					
Innovative Approaches to Characterize Vadose Zone Hydraulic Properties		P					
Computing Framework for Environmental Cleanup, Restoration, and Long-Term Stewardship		P	S				
Decontamination, Decommissioning, and Remediation of Optimal Planning System for the Advanced Decontamination and Decommissioning System					P		
Waste Characterization and Sorting Station for the Advanced Decontamination and Decommissioning System					P		
Robotic Waste Packaging System for the Advanced Decontamination and Decommissioning Systems					P		
Environmental Separations and Barriers	S	P	S				
Proton Conducting Ceramic Membrane Applied to Spent Nuclear Fuel Stewardship		P	S				
Spectroscopic Investigations at Solid Supercritical Fluid Interfaces in Support of Advanced Supercritical Separation Techniques	P						

R&D Capability Development

Prior to ESRC, INEEL R&D capabilities were categorized into 49 R&D capabilities, grouped into nine discipline areas. We used this scheme to assess which capabilities and disciplines were being enhanced to the ESRC Program. Most of the 9 discipline areas will be improved by ESRC research. The disciplines primarily supported are as follows:

- Applied Engineering
- Biotechnology
- Chemistry and Chemical Engineering
- Earth Science
- Information Management Technologies

There are a few tasks that improve capabilities in the disciplines of Material Science and Technology, Nuclear Science and Technology, and Sensing and Diagnostics. No task was particularly relevant to the discipline of System Engineering.

We find that two-thirds of the 49 INEEL R&D capabilities will be improved by ESRC research (see Table C-2). The capabilities primarily supported are as follows:

- Environmental monitoring
- Groundwater hydrology and hydrochemistry
- Vadose zone hydrology and soil physics
- Modeling, simulation, and information visualization
- Environmental engineering
- Geophysics, property characterization
- Surface hydrology and land use
- Engineered systems.

Of these eight capabilities, six are in the Earth Science discipline. This is expected, since two of the four ESRC research areas are “Environmental Characterization Science and Technology” and “Subsurface Understanding.”

The ESRC area, “Scientific Environmental Simulation,” puts “modeling, simulation, and information visualization” on the above list. Indeed, the associated advanced computational capability and techniques assists a broad range of capabilities in the disciplines of applied engineering, earth science, and information management technologies.

The ESRC area, “Environmental Systems Science and Technology” contributes to several capabilities in the applied engineering and chemistry/chemical engineering disciplines.

Table C-2. ESRC portfolio contribution to INEEL research capabilities.

Discipline	Applied Engineering					Biotechnology				Chemistry and Chemical Engineering						Earth Science					Information Management Technologies						
	Applied math and statistics	Engineered systems	Human factors	Process control systems	Robotics (other engineering)	Environmental microbiology	Extremophile biology	Biogeochemistry, subsurface biology	Molecular genetics & genomics	Bioprocessing systems	Analytical chemistry	Biochemistry	Computational chemistry	Environmental surface chemistry	Inorganic chemistry	Separation chemistry & selective mass transport agents	Supercritical fluid chemistry	Ecological monitoring	Environmental engineering	Geology	Geophysics, property characterization	Groundwater hydrology and hydrochemistry	Surface hydrology & land use	Vadose zone hydrology & soil physics	Enterprise computing in support of DOE missions	General information technology research and development	Modeling, simulation, information visualization
Technical Capability																											
Nondestructive Assay Science and Technology Proof-of-Concept Testing for Environmental Characterization and Stewardship		X																X									
Assessment of Mercury Environmental Fate and Transport from INEEL Waste Processing Facilities for Long-term Stewardship Concerns and Development of Improved Modeling Methods																		X					X				X
Ion Mobility Spectrometry for Environmental Monitoring and In Situ Measurement of Hazardous Organics						X	X			X				X				X				X					
Molecular Engineering and Genomics for Development of Environmental Biosensors Using Robust Biocatalysts				X		X	X	X	X	X	X	X		X				X				X					
Biologically Based Catalysts for Processing and Detection in Harsh Service Environments				X		X	X	X	X	X	X	X		X				X				X					
Wide-Area Moisture Sensing and Mapping																							X	X			
Advanced Robotic Technologies for Remote Environmental Surveillance and Stewardship	X	X		X														X		X		X	X	X			
Isobaric Groundwater Well for Precise Water Level Measurement Relevant to Long-Term Surveillance and Stewardship																		X				X		X			

Discipline	Applied Engineering					Biotechnology				Chemistry and Chemical Engineering						Earth Science					Information Management Technologies							
	Applied math and statistics	Engineered systems	Human factors	Process control systems	Robotics (other engineering)	Environmental microbiology	Extremophile biology	Biogeochemistry, subsurface biology	Molecular genetics & genomics	Bioprocessing systems	Analytical chemistry	Biochemistry	Computational chemistry	Environmental surface chemistry	Inorganic chemistry	Separation chemistry & selective mass transport agents	Supercritical fluid chemistry	Ecological monitoring	Environmental engineering	Geology	Geophysics, property characterization	Groundwater hydrology and hydrochemistry	Surface hydrology & land use	Vadose zone hydrology & soil physics	Enterprise computing in support of DOE missions	General information technology research and development	Modeling, simulation, information visualization	
Technical Capability																												
Secondary Ion Mass Spectrometry Characterization of Environmental Microbial Processes						X	X		X	X				X				X				X						
Using Environmental Records in Mid-Latitude Glacier Ice to Better Define EM Contaminant Inputs to the Subsurface																		X					X					X
Geological, Geophysical and Hydrological Environs of the INEEL Site																		X	X		X		X					
Complex Systems Theory Applied to Subsurface Transport	X																	X		X	X		X					X
Ecological Engineering of Rhizosphere Systems		X				X	X	X	X										X									X
Investigation of Factors Influencing Cesium Mobility and Update in Plant/Soil Systems		X				X	X	X	X										X									X
Long-Term Biogeochemical Destruction and Control of Aquifer Contaminants Using Single-Well Push-Pull Tests		X				X	X	X										X	X			X						
Unified Hydrogeophysical Parameter Estimation Approach to Subsurface Contaminant Transport—Subsurface Imaging Collaboration with the Center for Subsurface Sensing and Imaging Systems																		X		X	X	X	X					X
Innovative Approaches to Characterize Vadose Zone Hydraulic Properties																		X			X			X				

