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CORE CAPABILITIES AND TECHNICAL ENHANCEMENT FY-1998 ANNUAL REPORT

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Core Capabilities and Technical Enhancement, FY-98 Annual Report

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ABSTRACT

The Core Capability and Technical Enhancement (CC&TE) Program, a part of the Verification, Validation, and Engineering Assessment Program, was implemented to enhance and augment the technical capabilities of the Idaho National Engineering and Environmental Laboratory (INEEL). The purpose for strengthening the technical capabilities of the INEEL is to provide the technical base to serve effectively as the Environmental Management Laboratory for the Office of Environmental Management (EM). An analysis of EM's science and technology needs as well as the technology investments currently being made by EM across the complex was used to formulate a portfolio of research activities designed to address EM's needs without overlapping work being done elsewhere. An additional purpose is to enhance and maintain the technical capabilities and research infrastructure at the INEEL.

This is a progress report for fiscal year 1998 for the five CC&TE research investment areas: (a) transport aspects of selective mass transport agents, (b) chemistry of environmental surfaces, (c) materials dynamics, (d) characterization science, and (e) computational simulation of mechanical and chemical systems. In addition to the five purely technical research areas, this report deals with the science and technology foundations element of the CC&TE from the standpoint of program management and complex-wide issues. This report also provides details of ongoing and future work in all six areas.

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Core Capabilities and Technical Enhancement, FY-98 Annual Report

INTRODUCTION

The Core Capability and Technical Enhancement Program (CC&TE), a part of the Verification, Validation, and Engineering Assessment Program (VV&EA), was implemented to enhance and augment the technical capabilities of the Idaho National Engineering and Environmental Laboratory (INEEL). The purpose for strengthening the technical capabilities of the INEEL is to provide the technical base to serve effectively as the Environmental Management Laboratory for the Office of Environmental Management (EM). Similar programs have existed for some time at Defense Program (DP) laboratories such as Sandia National Laboratory and Los Alamos National Laboratory.

Since the CC&TE program is intended to strengthen the INEEL's ability to respond to EM's technical needs and issues, an analysis of EM's needs and issues was performed prior to deciding on which technical areas to focus. In addition a survey of basic science and technology development activities being funded by the EM Focus Areas and the EM Science program was undertaken. This was done in order to prevent duplication within the CC&TE program of existing EM-supported research. Six areas were identified for investment (see Figure 1). Five of these are purely technical, and the sixth deals with programmatic and complex-wide issues of research/technology analysis, integration, and program management. A brief description of the five research areas follows.

Transport Aspects of Selective Mass Transport Agents

This research area has three tasks:

Selective Mass Transport in Polymers

Chemical separations are frequently used throughout EM. Separations often involve unique materials due to highly aggressive thermal and chemical environments and also to the presence of high levels of radiation. Typical organic materials do not maintain structural integrity in these types of environments. Inorganic polymers offer both greatly enhanced durability coupled with synthetic versatility; thus they have been selected as models for study to determine the nature of the interactions between transported chemical species and solid polymer matrices. Specific separations materials were tailored to include highly basic media similar to that in the tank farms at the Hanford Site and highly acidic environments such as those at the INEEL. In this study, the separations performed were ethylene diamine/water as a model for high pH basic aqueous environments and water/organic dye as a model for neutral organic-water feed streams as a dewatering process.

Pore Size and Morphology Control for Solid and Polymer Matrices

Hybrid organic/inorganic materials offer greatly enhanced durabilities and thus have been chosen for studying interactions between potential permeants and these materials. Specific separations materials are being tailored for environments such as those in the highly basic media at the tank farms at the Hanford Site and highly acidic environments such as those at the INEEL. Models for these separations include organic/water separation of light organics, i.e., TCE or methylene chloride from water; ethylenediamine/water separations that simulate basic conditions such as those in Hanford tank waste; and lithium ion transport to simulate transport of radionuclides such as strontium and cesium.

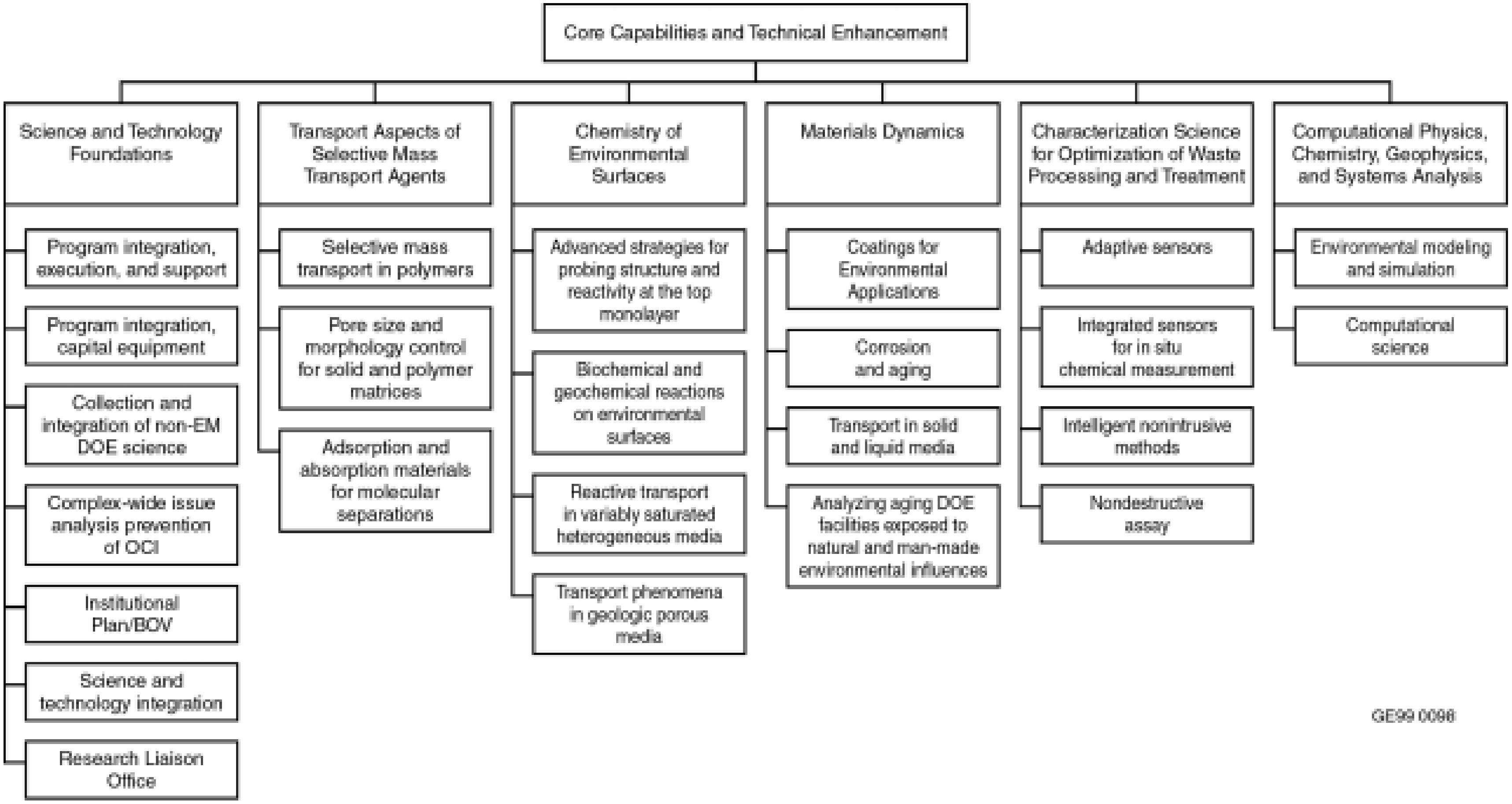

Figure 1. Core capabilities and technical enhancement work breakdown structure.

Adsorption and Absorption Materials for Molecular Separations

Contaminants can be removed from a waste or process stream by separation and/or conversion processes. The focus of this task was developing novel materials that allow separation of EM-focused pollutants from gaseous and liquid sources. Such materials are engineered to have surface sites and/or meso porosity conducive to retaining incident target molecules. Both inorganic and organic materials can be used, e.g., polymer-based ion exchange resins, polyphosphazenes, zeolites, activated oxides, and activated carbon. This task is to investigate processing mesoporous copper sulfides with a propensity for mercury intercalation from gaseous sources.

Chemistry of Environmental Surfaces

This research area has four tasks:

Advanced Strategies for Probing the Structure and Reactivity of the Top Monolayer

The objective of this program is to understand the reaction dynamics of adsorbate (or contaminant) molecules with metal oxide surfaces, and in so doing build THE INEEL capability in the area of surface chemistry. The scope for this program encompasses two tasks for FY 1998:

Investigating aluminosilicate oligomeric anions and their reactivity. This includes development and application of secondary ion mass spectrometry (SIMS) methods for characterizing adsorbate species on surfaces. Secondly, it includes developing the staff and instrumental capability that will permit application of novel surface interrogation approaches to the chemistry of significant contaminant-surface systems.

Biological and Geochemical Reactions on Environmental Surfaces

The objective of this task is to develop a set of analytical of methods for determining chemical speciation and reaction mechanisms affecting the interaction of selected contaminants and biologicals with relevant surfaces under “ambient” conditions. The development of techniques and methodologies only serves a useful purpose if they can be applied to the investigation of real problems. These methods are expected to help resolve a number of questions about environmental surface chemistry that have not been accessible to date. The new methods will be applied to a range of specific problems with relevance to DOE-EM and issues in environmental science. The work involves a strong collaboration between chemists, microbiologists, and geochemists.

Reactive Transport in Variably Saturated Media

This task is to improve understanding of how contamination migrates through the vadose zone, which is the region between the earth’s surface and the underlying water table. Four subtasks were established for FY 1998: up-scaling of geochemical heterogeneity, propagation of geochemical environment in the vadose zone, integrated vadose zone characterization, and enhanced computational methods.

Transport Phenomena in Geologic Porous Media

Five research subtasks make up this task.

Partitioning of bacterial populations between mobile and immobile phases in saturated basalt is one subtask. Its objective is to improve the ability to predict the location of microbial biomass and functions in saturated subsurface environments.

Computational modeling of microbial processes and chemical transports is the second subtask. Its objective is to address the fundamental question of how laboratory studies can fail to predict the behavior of a biodegraded plume in the field.

Utilization of deep tensiometers to interrogate and validate numeric models and existing field data is the third subtask. Its objective is to collect, interpret, and integrate soil water potential data to improve the understanding of deep vadose zone transport based upon field measurements.

Steam-enhanced extraction in fractured porous media is the fourth subtask. Its objective is to conduct experiments that model steam condensation front position, velocity, and temperature profile during the steam-enhanced extraction process of removing liquid contaminants in fractured porous media.

Saturated zone testing of biologically mediated actinide transport in the subsurface is the fifth subtask. Its objective is to better understand the coupling of microbial processes and surface geochemical reactions that affect the migration of actinides such as plutonium and uranium through unsaturated and saturated zones in the subsurface.

Materials Dynamics

This research area consists of four tasks:

Coatings for Environmental Applications

This task addresses plasma-sprayed protective coatings for high temperature process equipment for EM applications. The objective is to understand the relationship of the in-flight particle characteristics (size, temperature, and velocity) to the microstructure and properties of the coating. In addition to the process variables, the role of surface preparation methods on residual stress and bonding is being examined for model ceramic and metallic coatings on steel substrates using numerical simulation and experiments. Methods are being developed to measure adhesion between the coating and the substrate, and the mechanical and physical properties of the coatings will be related to the processing conditions.

Corrosion and Aging

Biologically induced or assisted corrosion has been reported, but little is known about the fundamentals of the process. This project is to examine the potential of microorganisms to establish biofilms on structural alloys that are significant to the interim and long-term storage of spent fuel and nuclear waste. Secondly, it is to do fundamental studies of microorganisms in extreme environments that are representative of those of interest to DOE. Examples are environments with high temperatures and pressures, radiation fields, etc.

Transport in Solid and Liquid Media

Transport phenomena are a primary scientific concern of environmental and waste management. Examples include pollutant seepage through fractured rock to an underlying aquifer; spread of decay heat from buried radioactive wastes that may induce deleterious phase transformations in the containment material; flow of electrical current in waste vitrification; and diffusion and trapping of contaminant molecules in porous membranes. In every case, the flux occurs as a result of an applied field; these are connected by the transport coefficient, which in general is a second-rank tensor.

Calculation of the transport coefficient is the focus of this research project. This is a very difficult task because of the extreme sensitivity of the measured value of the transport coefficient to the geometry of the medium. For example, the tortuosity of the conducting paths through a conductor–insulator composite is the primary determinant of the effective conductivity of the material, while the actual volume fraction of conductor has lesser influence. Thus this research project must develop useful statistical descriptions of geometrically complex materials in addition to methods for calculating effective values for transport coefficients.

Analyzing Aging DOE Facilities Exposed to Natural and Man-Made Environmental Influences

This task is to develop a research-based life-cycle management engineering model that will provide THE INEEL and DOE with a tool for estimating life-cycle costs for THE INEEL structures. Roof systems present one of the most common repair/replace expenses at all THE INEEL facilities, so roofing systems are the focus of this task. The roof management life-cycle engineering model is to establish a relational database specific to the INEEL, providing guidance to designers, inspectors, facility managers, and operations personnel in making roof system choices based on THE INEEL weather, materials issues, facility use, facility design, and prior inspection data. The model design permits updating of all input data as more accurate data become available.

Characterization Science

This research area has four tasks:

Adaptive Sensors

Nonlinear optical methods offer an imaging solution to DOE-EM sensing problems. Optics has been chosen as the basic mechanism by which the information to be measured is transferred to the sensor because it is noncontacting, suitable for industrial environments, and has “full-field” imaging capability. In addition to sensing data as images, nonlinear optics can perform mathematical image processing and can perform operations that allow for, or adapt to, data and/or interfering (noise) signals. Such adaptive mechanisms are very important for field use. Phase modulation can be used to record surface profile, deformation, vibration, and ultrasonic motion; it can also be used to record changes in optical wavelength leading to applications such as photoacoustic spectroscopy for material property, surface contamination, and trace gas analysis. This task is researching applications of adaptive sensing to aspects of environmental monitoring. The first year’s results show that the nonlinear optical effect in certain materials, when configured for dynamic holographic sensing, can produce sensors that are self-adaptive, self-processing, and highly sensitive, with wide area imaging in real-time.

Integrated Sensors for In Situ Chemical Measurement

This task has an overall goal of carrying out research that will provide the basis for new instrumentation or methods by which environmental chemical measurements can be made. One of the principal objectives for the program is creation of instrument concepts that allow for development of smaller instruments that are easier and/or less costly to take into the field. There are also opportunities for instrumentation with these properties to have an impact in the area of process monitoring.

The range of detection methods being employed in this research includes optical measurements, ion current measurement, and surface acoustic waves. Several means are being explored to enhance the sensitivity and selectivity of these detection methods. These include membrane separation for microsamplers and sample conditioning as well as fluorescence tagging with analyte specific biological species.

Intelligent Nonintrusive Methods for Characterization

This task addresses several basic physics and data processing issues in characterization of spent nuclear fuel (SNF) and other nuclear waste and industrial inspection problems. Successful nonintrusive inspection often involves making a series of independent measurements and applying prior knowledge, intelligent processing of information, and automated decisionmaking. This project is studying two independent nonintrusive technologies, eddy current and x-ray imaging, and several approaches to data interpretation with the overall objective of advancing the state of the art in nonintrusive sensing and intelligent data processing while enabling specific improvements to spent nuclear fuel inspection, transuranic (TRU) waste characterization, and industrial inspection.

Specific objectives include developing a greater understanding of potential spent fuel inspection/characterization problems and making advances in intelligent processing of waste characterization data. The studies in this project are to resolve characterization issues, select specific characterization problems to approach, investigate the unique physical phenomena affecting the measurements, develop selected sensors, and develop interpretation and processing algorithms. There are four specific tasks: spent nuclear fuel characterization issues, intelligent interpretation of waste characterization data, electromagnetic material characterization, and imaging in constrained environments.

Nondestructive Assay

Nondestructive assay (NDA) has long been a major part of the INEEL core technologies. As a result of a strong commitment to fundamental nuclear and neutron physics research coupled with a strong application effort, this laboratory has established an international reputation in fundamental and applied gamma ray spectrometry and neutron-based assay methods. This NDA research task is to build on the existing technology base and perform research related to radio-assay signatures for elemental identification and quantification.

Computational Simulation of Mechanical and Chemical Systems

This research area has two tasks:

Environmental Modeling and Simulation

This task is to produce a robust, effective and modern set of computing technologies to support modeling and simulation of computational components of environment problems. The charter includes support for all elements of computational work including physical and process simulation, data analysis, and archiving along with appropriate visualization and communication tools.

Computational Science

EM soon will be making expensive and long-lasting choices from among a wide range of new technologies, processes, or strategies for remediation, alternative manufacturing processes and products, and stewardship of legacy wastes, among others, as part of its obligation to manage environmental issues.

The computational science project is intended to give EM the ability to make informed choices among the variety of proposals for the disposition of waste. The ultimate goal is the trustworthy, even if only qualitative, prediction of the outcome of a wide variety of proposed technologies, processes, or strategies that might be employed in environmental management. Secondarily, we might also be able to propose improved solutions for environmental problems.

Science and Technology Foundations

This sixth and final element is primarily nontechnical and has four tasks that are directed toward both the INEEL and complex-wide research and technology analysis and integration issues:

Collection and Integration of Non-EM DOE Science

This program identified software needs for four areas of environmental research at the INEEL and found sources, within and without the DOE Laboratories, for that software. The areas are:

- Calculation of steam condensation front propagation during steam-enhanced extraction to remove volatile or semivolatile organic contaminants in fractured porous media

- Computer simulation for imaging situations that arise in characterization of spent fuel containers or operator/radiographer training for radioactive waste characterization

- Environmental modeling on Beowulf-type commodity supercomputers.

- Development of the conceptual framework for integrating components being developed by other DOE labs, federal agencies, and the scientific community into a decision support system for future management of DOE lands. Completing the full scope of this effort will take two to three years.

Issue Analysis and Resolution Throughout the DOE Complex

This effort is to develop methods for unbiased assessment and resolution of issues facing DOE-EM. It is to identify and resolve significant roadblocks preventing solution to complex-wide EM issues. It seeks to identify a set of EM issues relating to THE INEEL core capabilities and roadblocks that could have a long-term impact on our ability to produce system-wide solutions for EM.

The following project activities were planned:

- Review literature concerning neutral facilitation, arbitration, and honest brokerage theory and practice.

- Review public information about structures and practices of organizations that consider themselves honest brokers.

- Review issues and problems facing DOE and THE INEEL that may require honest broker assistance for successful completion.

- Select best practices of organizations that are considered exemplary in carrying out honest broker functions.

- Develop a definition and theory of honest brokering that can guide the development of capabilities for honest brokering at the INEEL.

Science and Technology Integration

The primary objective of the Science and Technology Integration task is the creation and use of a system by which the DOE-EM's unaddressed fundamental science needs can be effectively met by the CC&TE program's research and development activities. This includes analysis of the technology and science needs developed by EM complex-wide operations activities as well as analysis of ongoing research efforts sponsored by EM. These data are used to validate and enhance the CC&TE program's research portfolio.

Research Liaison Office

The specific objective of this project is to establish a research liaison function to coordinate and assist with the conduct of environmental research at the INEEL. The functions of this liaison are to: develop guidelines, or a decision tree, for how researchers will comply with site access, sample handling, and safety (environmental and personal) requirements while conducting work at the INEEL or with THE INEEL samples; to act as a single point of contact between researchers and THE INEEL ES&H, SMO, facilities, EM project personnel; and to document the resource requirements (cost and time) for conducting research at the INEEL.

One of the primary objectives in enhancing and maintaining the INEEL's technical capabilities is to strengthen its ability to address EM's technical and science-based issues. For that reason the research portfolio sponsored under the CC&TE program was formulated in a way that created a high degree of EM relevancy. The research activities being conducted within the various tasks that comprise each of the research areas described above have been compared to various needs data generated by EM. Basic science needs and technology development needs generated by the Site Technology Coordination Groups (STCGs), associated with each of the field offices, as well as data from the EM Integration activity, and the 2006 Paths to Closure documents have been used to supply the data for this comparison. Each of the ongoing research activities can be tied to one or more of the needs from the EM data.

The CC&TE program was funded only a little more than seven months before the creation of this report. The following sections will describe in detail what we consider to be outstanding progress in light of the short duration of the program.

SELECTIVE MASS TRANSPORT IN POLYMERS

F. F. Stewart

Scope and Objectives

Chemical separations are frequently used throughout the Department of Energy's Office of Environmental Management. Separations often involve unique materials due to highly aggressive thermal and chemical environments and also to the presence of high levels of radiation. Typical organic materials do not maintain structural integrity in these types of environments. Inorganic polymers offer both greatly enhanced durability coupled with synthetic versatility; thus they have been selected as models for study to determine the nature of the interactions between transported chemical species and solid polymer matrices.

Specific separations materials were tailored to include highly basic media similar to what is found in the tank farms at the Hanford Site and highly acidic environments such as those found at the INEEL. In this study, the separations performed were ethylene diamine/water as a model for high pH basic aqueous environments and water/organic dye as a model for neutral organic-water feed streams as a dewatering process.

There were three tasks for FY 1998.

1. Study linear phosphazenes and determine how they can be tailored to provided enhanced physical and chemical properties. Included is utilization of methodologies for providing chemoselectivity and controlled morphology in thin-dense films.

2. Develop chemoselective phosphazene-based cyclomatrix polymers that have an increased level of polymerization control as compared to the ubiquitous linear phosphazene polymer family.

3. Develop a computer-based modeling capability that can accurately describe the interaction of permeates with substrates. Use this to model gas transport through selected polymer membranes to understand solubility, a key parameter in determining and predicting transport.

Technical Accomplishments

Background

An understanding of the chemical interactions that occur between a permeate and a solid matrix is the key to developing highly efficient separation processes employing membranes or barriers. A membrane can be thought of as a macromolecular network that, either through chemical affinity or through free volume in the matrix, will permit the transport of a finite chemical species while a barrier prevents transport. FY 1998 work focused on polymeric materials for use in a variety of EM-related needs. In the first year of this study a system of model polymers—polyphosphazenes—was chosen for examination. The rationale behind this decision was based on several factors including their synthetic variability, literature precedent for these materials to be used as separation media, and their well-known resistance to extreme chemical and thermal environments, and radiation induced decay.

Linear polyphosphazenes, as a model polymer system, are unique due to the fact that they can be synthesized with a vast array of potential physical and chemical characteristics. Typical phosphazene materials range from water-soluble[1] to water insoluble,[2] elastomeric to glass-like,[3] and fluid[4] to solid.[5] Crystallinity varies from amorphous to crystalline.[3] Conditionally, these linear polymers have been reported to be stable, in a bulk form, to temperatures up to 300°C.[3] Most importantly, the radiation stability of these polymers far exceeds organic polymers, thus these materials are ideal for model studies. The unique character of these polymers is provided by two major influences. First, the backbone consists of alternating phosphorus and nitrogen atoms with alternating double and single bonds. The bonding in these systems leaves pi-electrons delocalized between phosphorus atoms but not across them; thus these materials are not conductive. However, the phosphorus atoms are pentavalent with initially polymerized material substituted by chlorine. Chlorine-phosphorus bonds in these materials are highly labile; thus polydichlorophosphazene is hydrolytically unstable. Stabilization of the backbone has been reported extensively by the reaction of polydichlorophosphazene with organic[6] or organometallic[7] nucleophiles. The nature of these substituents, or pendant groups, dictates the chemoselectivity of derived materials. For example, attachment of water-soluble 2-(2-methoxyethoxy)ethanol (MEE) to the phosphorus-nitrogen backbone yields a polymer that is also water-soluble and can only be made insoluble by extensive crosslinking.[8] Likewise, hydrophobic groups such as phenoxide can impart water insolubility. Pendant groups also dictate the crystallinity of the resulting polymer. Specific polymeric species were synthesized and studied to observe interactions with transported species. Additionally, novel methods for forming these polymers into highly stable, chemically resistant materials were developed.

Linear polyphosphazenes are most commonly synthesized using the ring opening polymerization of the commercially available hexachlorocyclotriphosphazene.[9] The chemistry of hexachlorocyclotriphosphazene is in many ways very similar to that of linear polydichlorophosphazene. Substitution of chlorine with organic nucleophiles gives stable solid materials. Use of a mixture of nucleophile has been observed to inhibit crystallization yielding low volatility nonflammable fluids.[4] These materials also have been developed as polymeric structural composite materials where the phosphazene forms a high polymer with a cyclomatrix backbone, multiple cyclic phosphazene six-membered crosslinked together.[10] Synthetically, this process is difficult to control, which is necessary for separations materials. New methods of forming these potentially valuable materials were studied in this project.

An additional tool that has value in determining the specifics of intermolecular interactions between a polymeric substrate and a transported species is computer-based modeling. The literature is replete with theoretic determinations of the interactions of gasses with organic polymers.[11] Application of these methodologies to inorganic polymers has been explored to a lesser degree. The scope of this segment of the project was to utilize modeling as an additional tool to understand molecular permeation through polyphosphazene-based model separation materials. For validation of computer-based modeling, characterization of the polymer membranes is required and was investigated using gas transport behavior.

In addition to the intensive research into the fundamental aspects of polymer permeate interactions and transport for liquid systems, gas transport is another very important membrane application. Fortuitously, the same experiment that gives the permeability of a single gas also gives the solubility and diffusivity of that gas; these three parameters are key in understanding the types of interactions that are important in promoting permeate transport within the membrane. So a single type of experiment provides a unique way to further characterize the polymer permeate interactions. The objective of this subtask was to determine the permeabilities, diffusivities, and solubilities of a select set of polymers to several gases. The scope was limited to testing polymers with anomalously high free volumes, which showed increased permeabilities towards higher alkanes such as butane.

Task 1. Linear Polyphosphazenes as a Model for Durable Polymeric Separation Materials

The significant challenges within the DOE-EM legacy issues are a variety of aqueous wastes. Fundamental research was conducted to develop a polymeric system that would resist degradation in basic (pH >12) environments. The model separation chosen for these studies was the separation of ethylenediamine from water. The phosphazene model system has two major pathways for development. First, polymer pendant groups may be modified to match the desired chemical species to be transported. Second, the polymer morphology may be modified to enhance durability.

Linear phosphazene polymers were synthesized that contained a random distribution of three differing pendant groups: p-methoxy phenol for good film forming characteristics, 2-(2-methoxyethoxy)ethanol (MEE) for water solubility/selectivity, and ortho-allylphenol to allow for crosslinking. To characterize these materials for their ability to pass water, the polymers were cast and mounted in a pervaporation cell and a series of water-dye separation experiments were conducted, see Table 1. The composition of the polymer is given using percent hydrophilic MEE and percent aromatic. This aromatic term contains both the p-methoxyphenol and the ortho-allylphenol, the latter was measured at approximately 5% with the former constituting the balance.

Polymers were assessed for their hydrophilicity by a gravimetric determination of the mass of water that the materials absorb upon immersion. Good correlation is observed between the fluxes of water in the dye-water separation and the swelling experiment—the more the polymer swells the higher the flux. It also should be noted that there is a limit to the degree that increased swelling will give higher fluxes. At extreme degrees of swelling, structural rigidity of the polymer is compromised thus rendering the material useless because of poor durability.

Another significant feature is noted in the data presented in Table 1. It would be expected that the materials with the largest percentage of hydrophilic pendant group would have the highest fluxes for water. However this was not observed suggesting that there are other factors besides simple substituent composition that effect membrane transport.

Polymer molecular morphology may be modified by crosslinking and it is readily known that increased amounts of crosslinking will add durability to a polymer; however this usually comes at the expense of flux. Generally, swelling of, and flux through, a membrane decreases with increased crosslinking. Polymer lot #016 was crosslinked thermally at 130°C with benzoyl peroxide as an initiator and tested in a pervaporation cell with 20% aqueous ethylenediamine as the feed. Prior to crosslinking this polymer decomposes in this basic feedstream. After crosslinking, the polymer readily performed the separation without decomposition, see Table 2. This result showed the validity of crosslinking these materials to gain structural integrity and resistance to harsh chemical environments.

Table 1. Separation of water from a water-dye feedstream using pervaporation.

Lot #	% MEE	% Aromatic	Polymer swelling (%)	Flux, 52°C (L/m^2hr)
024	25	75	400	0.27
016	31	69	150	0.15
030	38	62	25	0.06

Table 2. Pervaporation testing of a crosslinked polyphosphazene in 20% aqueous ethylenediamine.

Polymer Lot #	Flux (L/m^2hr)	Temp (°C)	Separation factor (% Rejection)
016	0.11	35	92
016	0.14	38	84

Crosslinking of polymers occurs through carbon-carbon bond forming processes driven by free radical chemistry. Free radicals may be generated thermally or through the use of UV irradiation. These types are usually performed with an initiator that undergoes homolytic bond cleavage when exposed to the excitation force. These free radicals then propagate through the polymeric matrix until termination. Electron beam radiation is also extensively used to cure or crosslink polymers, although the literature reports of this type of crosslinking using polyphosphazenes are few.[12] From a membrane formation standpoint, this type of crosslinking is attractive because of the expectation of a homogeneous crosslink density throughout the polymer film due to complete penetration without attenuation.

To benchmark electron beam crosslinking, a hydrophobic phosphazene terpolymer (PPXP) was chosen because of the extensive amount of characterization previously performed on this polymer. This polymer contains three differing pendant groups consisting of *p*-methoxyphenol (55%), *p-sec*-butylphenol (36%), and *o*-allylphenol (9%). Each of these pendant groups performs a separate function for the polymer. First, the *p*-methoxyphenol gives the material good film forming characteristics. Second, *p-sec*-butylphenol gives the polymer good elastomeric properties, and finally, *o*-allylphenol provides the ability to crosslink. This polymer is highly efficient as a membrane for separating chlorinated organics from water, an EM-relevant separation.

Electron beam crosslinking experiments revealed a positive correlation between crosslink density and dose, see Table 3. These experiments were performed on bulk polymer with an approximate 0.5 cm^3 volume. Estimation of the crosslink density was performed using standard Flory-type relationships that correlate swelling to crosslink density. Generally, as the crosslink density increases, the ability of the polymer to swell in a good solvent decreases due to extensive inter-chain bonding. Extents of polymer swelling were determined gravimetrically using acetone solvent, where the polymer is soluble prior to crosslinking. Additionally, it should be noted that the crosslink density indicates that crosslinking occurs through more groups than just the *o*-allylphenoxy pendant groups since the high level of crosslinking exceeds the amount of available *o*-allylphenol. At this time, it is proposed that the *p–sec*-butylphenol pendant groups also participate in crosslinking through the benzylic position.

To contrast the above-described electron beam crosslinking methodology, a commonly used thermally induced free radical process was employed. This process requires the use of a thermal initiator of free radicals within the polymeric matrix to perform crosslinking. Benzoyl peroxide, which decomposes to form free radicals at 106°C, was doped into bulk polymer at 1% (wt%).

Experiments were conducted at 130°C, 150°C, 170°C, and 190°C. Samples of polymer were heated for varying lengths of time to determine the time dependence of heating on crosslink density. At 130°C, crosslinking is observed to occur after approximately 10 minutes heating time with no appreciable increase in crosslink density with additional time, see Table 4. At higher temperatures, similar data were obtained, see Table 5. One general trend that was noted was an increase in solubility of polymer processed at 190°C suggesting a competing pathway of thermal polymer degradation. It is known that many phosphazenes are stable to 300°C in the macroscopic sense where no loss of material is observed on heating. However, there is literature precedent for chain scission processes at lower temperatures.

Table 3. Electron beam crosslinking of PPXP and estimation of crosslink density.

Electron Beam Dose	Solubility	Mers/Crosslink[a]	Crosslink Density (э)
5	78.3%	5.2	1.5×10^3
10	16.0%	3.4	2.3×10^3
15	7.6%	3.0	2.5×10^3
20	6.1%	2.7	2.8×10^3

a. Molecular weight of one mer = 321.4 g/mole, calculated from the percentages of each pendant group on the polymer.

Table 4. Solubilities, mer/crosslink values, and crosslink densities (э) for thermally induced free radical crosslinked PPXP at 130°C.

Heating Time (min)	Solubilities	Mers/Crosslink[a]	Crosslink Density (э)
5	100%	Dissolved	Dissolved
10	13.6	3.2	2.4×10^3
15	14.1	3.4	2.2×10^3
20	16.4	3.3	2.3×10^3
40	20.1	3.5	2.2×10^3
60	21.6	3.5	2.2×10^3
90	22.6	3.5	2.2×10^3

a. Molecular weight of one mer = 321.4 g/mole, calculated from the percentages of each pendant group on the polymer.

Table 5. Solubilities, mer/crosslink values, and crosslink densities (э) for thermally induced free radical crosslinked PPXP at 150°C, 170°C, and 190°C.

	Temperature150°C			Temperature170°C			Temperature 190°C		
Time (min)	Solubility	Mers/ Crosslink[a]	э	Solubility	Mers/ Crosslink[a]	э	Solubility	Mers/ Crosslink[a]	э
10	15%	3.2	2.4×10^3	18%	3.5	2.1×10^3	20%	3.5	2.2×10^3
20	22	3.9	2.0×10^3	23	3.8	2.0×10^3	33%	4.0	1.9×10^3
30	18	3.4	2.3×10^3	27	3.8	2.0×10^3	42%	4.2	1.8×10^3

a. Molecular weight of one mer = 321.4 g/mole, calculated from the percentages of each pendant group on the polymer.

Work performed at the conclusion of FY 1998 included the extension of this work to membranes with the ultimate goal of finding a correlation between crosslink density and separation factor/membrane flux. To date, 75 membranes have been prepared and crosslinked at various electron beam dosages. These materials are currently under study using standard thermal analysis and gravimetric swelling techniques to be followed by installation into pervaporation cells and tested with a variety of EM relevant feedstreams. Additionally, a manuscript currently is being written describing the findings presented here, submission to an American Chemical Society peer-reviewed publication, *Chemistry of Materials*, will occur by October 15, 1998.

Task 2. Development of Chemoselective Phosphazene Cyclomatrix Materials for EM-Relevant Separations.

There is a current need within EM for new lost-cost separation materials for extreme environments. Cyclomatrix phosphazene polymers offered a route for the facile and controllable synthesis of novel materials. This concept has a literature precedent[10] through the use of hydroxyl-functionalized hexaphenoxycyclotriphosphazenes, see Figure 1. Disadvantages of this synthesis are the high temperature employed to perform polymerization, 200°C, and the uncontrollable nature of the polymerization.

Soluble macromolecular materials can not be synthesized using this route. This potentially could be due to the reactivity of the hydroxyl functionality or the crosslinking agent. This fiscal year, we sought to use activated crosslinking agents while employing a lesser reactive phosphazene.

tert-Butylhydroquinone was found to react with hexachlorocyclotriphosphazene with regiospecificity giving the product, hexa-*tert*-butylhydroquinone cyclotriphosphazene in approximately 80% yield. Placement of *tert*-butyl groups ortho to the hydroxyl substituent serves two purposes. First, they hinder the hydroxyl groups, thus raising the activation energy barrier of reaction at that site. Second, the increased amount of aliphatic content to the trimer provided by the *tert*-butyl groups enhanced the material's solubility in common organic solvents. The synthesis of this trimer is novel and a manuscript was written and submitted to *Journal of Applied Polymer Science*.

As a proof-of-principle investigation, a series of crosslinking experiments were conducted using bifunctional aliphatic acid chlorides with the number of carbons ranging from four to twelve. These reagents had the potential to react with the hydroxyl functionality on the trimer to form an ester. All experiments were monitored through ^{13}C NMR spectroscopy. Initial experiments were conducted using tetrahydrofuran as the solvent with heating. NMR spectroscopy revealed that the reaction was facile, however poly(tetrahydrofuran) was observed in the reaction as a side product catalyzed by the reaction conditions. Changing the solvent to 1,4-dioxane prevented further unwanted side product formation. The reactions generally require heating up to the reflux temperature of 1,4-dioxane at 105°C to provide crosslinked product.

High polymers have been synthesized by this method. Molecular weights and polydispersities have been recorded using Gel Permeation Chromatography (GPC). Molecular weights of 300,000 were common with polydispersity indices noted at less than two. Correlations between experimental method and product have been observed and will be investigated more completely in the coming year. Molecular weights of product polymers are controlled by reaction stoichiometry. A large excess of acid chloride leads to lower molecular weight product while limiting the acid chloride causes the product molecular weight to increase. The reactions are not living polymerizations, thus once the supply of acid chloride is either exhausted or removed; polymerization ceases and generally cannot be re-initiated.

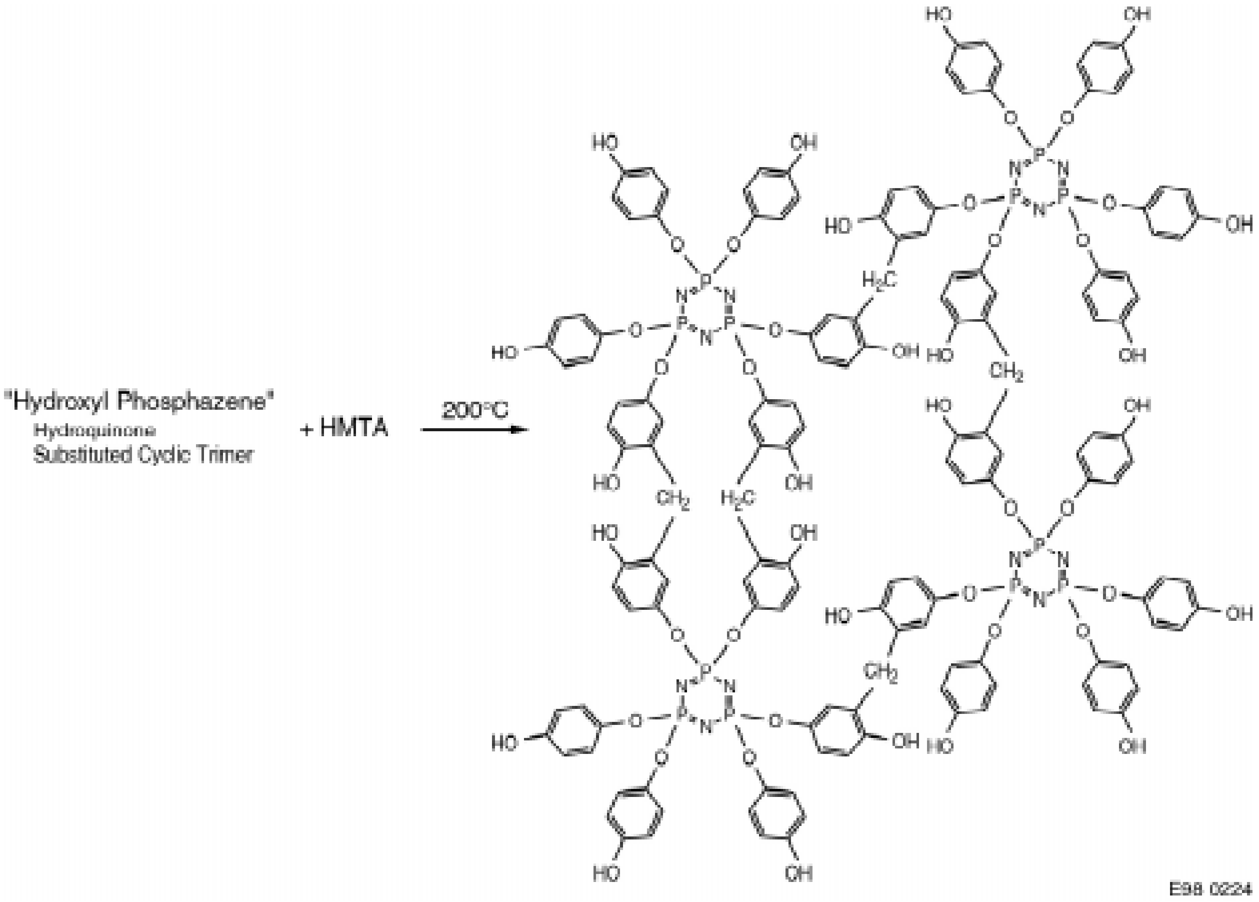

Figure 1. Synthesis of cyclomatrix polymer.

The major drawback of this technology is the instability of the ester linkage. Mild pH excursions either higher or lower than pH 7 will lead to hydrolysis of the ester linkages, thus leading to depolymerization. Exploitation of this new technology will require the development of more robust crosslinking methods such as isocyanates to form urethane-type linkages.

Task 3. Molecular Modeling and Gas Transport Studies

The experimental procedure involves exposing the membrane to a single (pure) gas and monitoring its permeation through the material. The 'pure' gas experiment is run by evacuating both sides of a membrane, isolating the cell from the vacuum, exposing one side of the film to the test gas, and monitoring the increase in pressure on the permeate side as a function of time. Typically, there is a period of time right after the experiment starts during which the pressure increase is nonlinear; but after a period of time when equilibrium transport is established, the pressure increase is linear. The linear portion of the pressure versus time plot yields the permeability and the nonlinear portion is a direct measure of the diffusivity. When these two values are known, then the solubility can be calculated by dividing the permeability by the diffusivity. A pure gas test apparatus was used to characterize a number of polymers in this manner.

Research performed during FY 1998 has led to the discovery that several formulations of phosphazene based polymers have nearly the same properties as a polymer called PTMSP (polytrimethylsilylpropyne). PTMSP has the highest free volume of any known polymer and the highest permeabilities to some gases. But PTMSP has severe stability problems when exposed to certain alkanes.

Three polymers were tested for pure gas permeabilities. They all have higher permeation rates for higher alkanes (butane) than for lower alkanes. Their permeabilities for butane are also higher than for other gases such as nitrogen, argon, helium, and even hydrogen. A fundamental understanding of the reasons for this performance could be valuable in designing better membrane based separations systems in the future.

When tested in the pure gas apparatus, it was determined that the solubility of the gases in the polymer was what was leading to the very high permeabilities. The high solubilities also contributed to the dissolution of the membrane film after a short period of time. To improve the stability of these materials, several membranes were cast and then exposed to electron beam radiation to promote crosslinking. The films have been received and are currently being evaluated.

Mathematical methods have been investigated during this effort in an attempt to describe gas solubility data within the model phosphazene polymers. For this effort, three levels of theory are directly applicable. First is Flory-Huggins/Hildebrand /Bicerano theory that allows for the rapid determinations of molecular interactions based upon a few empirical parameters. The second level is the application of Polymer Reference Interaction Site Model (PRISM) theory. This method is another rapid way to describe gas solubility within a polymer given an adequate force field. The third method is direct molecular dynamics that simulates movement of a permeating molecule within a polymer matrix. Generally, to perform this type of simulation requires much in the way of labor and computer resources. During FY 1998, the first two methods have been developed and applied to phosphazene polymers. The main problem encountered to this point has been the lack of data available to describe the phosphorus atom as found in the phosphazene polymer backbone. Efforts are underway to adapt these methods to phosphazenes by employing a force field that includes phosphorus. This force field found in COMPASS®, a relatively new software package for molecular modeling, is currently under investigation. Two manuscripts have been generated, submitted to the journal *Macromolecules,* and subsequently published in this portion of the project.

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PORE SIZE AND MORPHOLOGY CONTROL FOR SOLID AND POLYMER MATRICES

M. K. Harrup

Scope and Objectives

Chemical separations are frequently used throughout the Department of Energy's Office of Environmental Management. Separation often involves unique materials due to the highly aggressive thermal and chemical environments and also to the presence of high levels of radiation. Typical organic membrane materials do not maintain structural integrity in these types of environments. Hybrid organic/inorganic materials offer greatly enhanced durabilities and thus have been chosen for studying the interactions between potential permeants and these materials.

Specific separations materials will be tailored for environments such as those found in the highly basic media at the tank farms at the Hanford Site and highly acidic environments such as those found at the INEEL. Models for these separations include organic/water separation of light organics, i.e., TCE or methylene chloride from water; ethylenediamine/water separations that simulate basic conditions such as those found in Hanford tank waste; and lithium ion transport to simulate transport of radionuclides such as strontium and cesium.

There were two primary FY 1998 tasks:

1. Understand methods for generating enhanced durability polymer composite materials.

2. Create novel materials with controlled pore sizes for use as separations membranes.

Technical Accomplishments

Background

Part A: Molecular Composite Morphology Studies

Molecular composite materials are a relatively new development in the field of materials science.[1,2] These materials are hybrid organic/inorganic composite materials that are synthesized in a specific fashion resulting in a homogeneous final product. The advantages of such hybrid materials are that they possess properties that combine the beneficial aspects of both the organic and inorganic parent components. The organic component of these composites is a polymer of varying description and the inorganic component is a ceramic, typically silicates, although composites using titanates and zirconates are also known.[3] Early work with these composites focused on siloxane polymers,[2] but has since been expanded to include fluoropolymers,[4] polyphosphazenes,[5] and other types of organic polymers.

Formation of these molecular composites involves the condensation of ceramic precursors, such as tetraethylorthosilicate, (TEOS) *in situ* with a polymer dissolved in a solvent matrix compatible with the condensing ceramic. This condensation of ceramic precursors is commonly termed the sol-gel process[6,7] and has been used extensively in ceramics research to form materials with discrete pore sizes for separations applications.[8] The primary advantage gained by forming a material with the sol-gel process is the ability to use organic molecules as "templates" to fashion the ceramic pores. These "templates" are then removed by either washing or burning out the organic component leaving only the ceramic component behind.

With molecular composites, the organic “template” is purposefully left in the condensed ceramic to form the finished material. The result is materials that possess controlled pore sizes as dictated by polymer composition. But unlike the all-ceramic materials, molecular composites may be fashioned to overcome the disadvantages of ceramics as separations membranes, namely brittleness and a lack of chemoselectivity. Additionally, these molecular composites are superior materials to polymers alone as they overcome some of the problems associated with polymer membranes, namely durability and a lack of dimensional stability.

The objective of this study is to investigate methods of forming molecular composites into separations membranes, to assess their physical properties, and assess advantages gained over the parent polymer materials. To achieve this objective, the project’s work has focused upon two central strategies designed to accomplish EM-relevant separations. A pressing need is to separate mixed waste, which contain both RCRWD-listed hazardous organic chemicals and radioactive metal ions. To attack this problem, the following two strategies were designed to use molecular composites to achieve this type of separation.

The first strategy focused on generating controlled pore-sized, ion transmissive molecular composites and the characterization of their intrinsic properties, both physical and chemical. These membranes are designed to selectively pass metal ions while forming a barrier to light neutral organic species. For this effort, hydrophilic polymers were employed to form the molecular composites.

The second strategy focused on generating controlled pore-sized, ion blocking molecular composites and the characterization of their intrinsic properties, both physical and chemical. These membranes are designed to selectively pass light neutral organic species while forming a barrier to metal ions. For this effort, hydrophobic polymers were employed to form the molecular composites. Approaching the separations problem from both directions affords the opportunity to investigate the molecular interactions between the composite material and both the potential permeates simultaneously.

Part B: Solid Phase Controlled Pore Size Studies

Generation of materials based on small inorganic ring systems that are combined “all-inorganic” molecular composites possessing defined pore sizes were also a focus of these studies. Methods of making solid phases with controlled pore sizes (10 to 30Å) have been developed over the past 40 years and are well represented in both the patent and open literature.[9,10] Generally, they have included generating the pores with chemical templates. The chemical templates are then burned out of the solid structures during sintering leaving a porous structure with pores based upon the size and shape of the template molecule. An approach similar to that described in the previous section was investigated for forming these solid materials. This allows generation of pores with variable sizes based upon not only chemical composition, but also variables such as pH, salt concentration, and temperature. An intimate understanding of the molecular interactions has proven to be necessary to make this method work properly. Additionally, it is necessary to add specific functionality to the pores thusly generated providing a novel method for the development of new and different filters and membranes.

The objective in investigations of this nature was to form solid phase materials utilizing small inorganic ring systems linked together via a ceramic superstructure. These materials were unprecedented in the literature and experiments into the fundamental aspects of the synthesis of these materials, along with characterization of their physical properties, was the primary undertaking. Such materials possess many fewer organic components than the polymer molecular composites described in the previous section, and could serve as rugged ultrafilters for EM separations needs.

FY 1998 Accomplishments

Part A: Molecular Composite Morphology Studies

A family of phosphazene polymers was initially identified as the most promising for the successful formation of the relevant molecular composite materials. The polymers for these studies were chosen from a group of high performance polymers which were identified based both upon literature data and internal knowledge. These materials were designed to provide maximum interactions with the environment of interest for a specific separation (i.e., aqueous or organic). Polymers for each of the two separation strategies (*vide supra*) were synthesized and formed into polymer/silicate molecular composites. Subsequent characterization and testing protocols were so different that the investigations were divided into the two subtasks described below.

Subtask A) Ion Passing Polymer Composites. The chosen family of polymers for this subtask was one that incorporated small ether groups as a primary part of their ligand structure. This was deemed important for three reasons. First, polymers of this type are hydrophilic and known to pass metal ions.[11,12] Second, a representative polymer of this type, methoxyethoxyethoxy polyphosphazene (MEEP) was known in the literature[5] and could be used as a benchmark material to guide our initial synthetic efforts. The structure of this polymer is shown in Figure 1.

This polymer was the first one to be successfully formed into a molecular composite material in this lab. Third, the small ether moieties afford the opportunity for direct molecular condensation with the inorganic component of the molecular composite material. The exact nature of the bonding between the polymers and the ceramic is currently unknown. However, the following scheme (Figure 2) represents how direct covalent bonding between the condensing ceramic precursors and the polymer could occur.

Data collected from initial experiments with the first of the molecular composites suggests that a more intimate association than mere commingling of the ceramic and the polymer components. In these experiments, the MEEP molecular composites were swelled in THF and water, in which the parent polymer is readily soluble. After several days, the composite membranes were physically broken apart into tiny shards by sonication, centrifuged, and the supernatant liquid decanted off. Examination of this decantate revealed no traces of polymer dissociated from the composite structure. Further detailed examination of this system to quantify the extent of this covalent bonding is a priority for subsequent work.

In addition to this benchmark material, additional members of this polymer family were designed and synthesized. The synthetic rationale for the specific polymers chosen was two-fold. First, the polymers generated would be completely new materials and would provide further insight into the structure-property relationships of this family of polymers, useful for custom tailoring to specific applications. Second, the polymers possessed a variety of different ligand sizes that would potentially

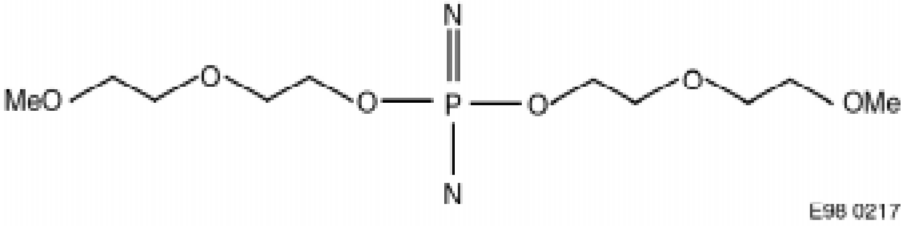

Figure 1. Structure of the MEEP polymer.

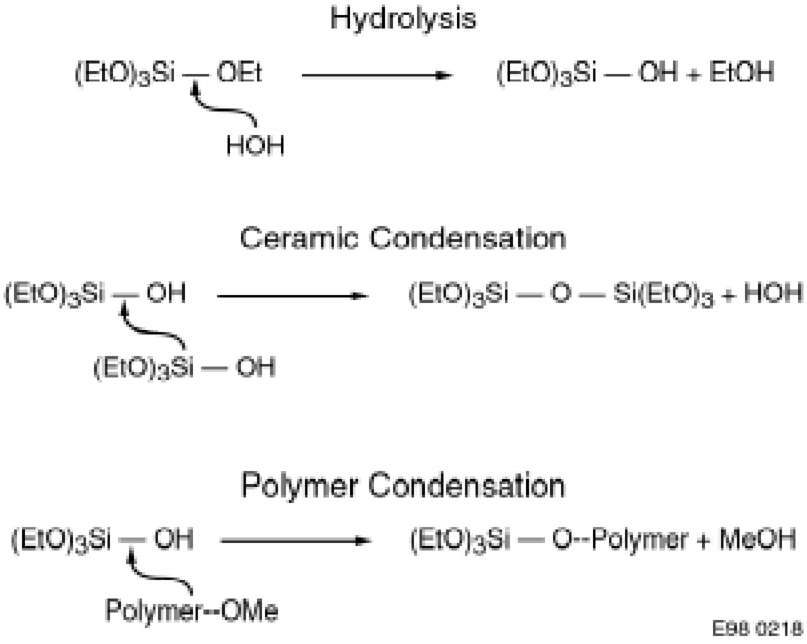

Figure 2. Condensation and potential bonding mechanisms.

lead to varied pore sizes in the finished materials. The new polymers that were generated were fully purified and subsequently characterized by NMR, thermal analysis methods—DSC, TGA, and elemental analysis. Their interactions with relevant solvents were also investigated. The specific polymers and their structures are shown in Figure 3.

Molecular composites have been successfully formed using these polymers in combination with the representative ceramic precursor tetraethylorthosilicate (TEOS). These new composite materials have been formed via the direct condensation of the ceramic precursor material *in situ* with a dilute solution of the polymer. The mixture is then cured for a period of several hours and then extensively dried to form the molecular composite. The final composition of the material is governed primarily by the ratio of polymer to condensed ceramic, and the resultant physical properties may be controlled to a great degree. The MEEP parent polymer, for example, is a viscous fluid when in its pure form, but composites have been formed that render the final material as an elastic rubber, or as a brittle solid.

These new composite materials have been evaluated in several different manners to determine both their characteristics and potential utilities to a variety of environmental applications. Thermal analysis of the materials has been completed, and this coupled with physical stability evaluations and mechanical analysis, forms the basis of the primary characterization methods available to study these new materials. Representative data from the thermal analysis of some of these composites is shown in Tables 1 and 2.

Table 1 shows the dramatic enhancement of durability achieved over the parent polymer by the addition of the ceramic component without sacrifice of the beneficial aspects of the parent polymer. The TGA data shows how easily solvent swelling, and hence loss of membrane integrity, is controlled, overcoming the parent polymer’s shortcomings. Similarly, the DSC data is evidence that the glass transition temperature is unaffected; thus the material retains its rubbery qualities overcoming ceramic brittleness and retaining ease of handling and processability.

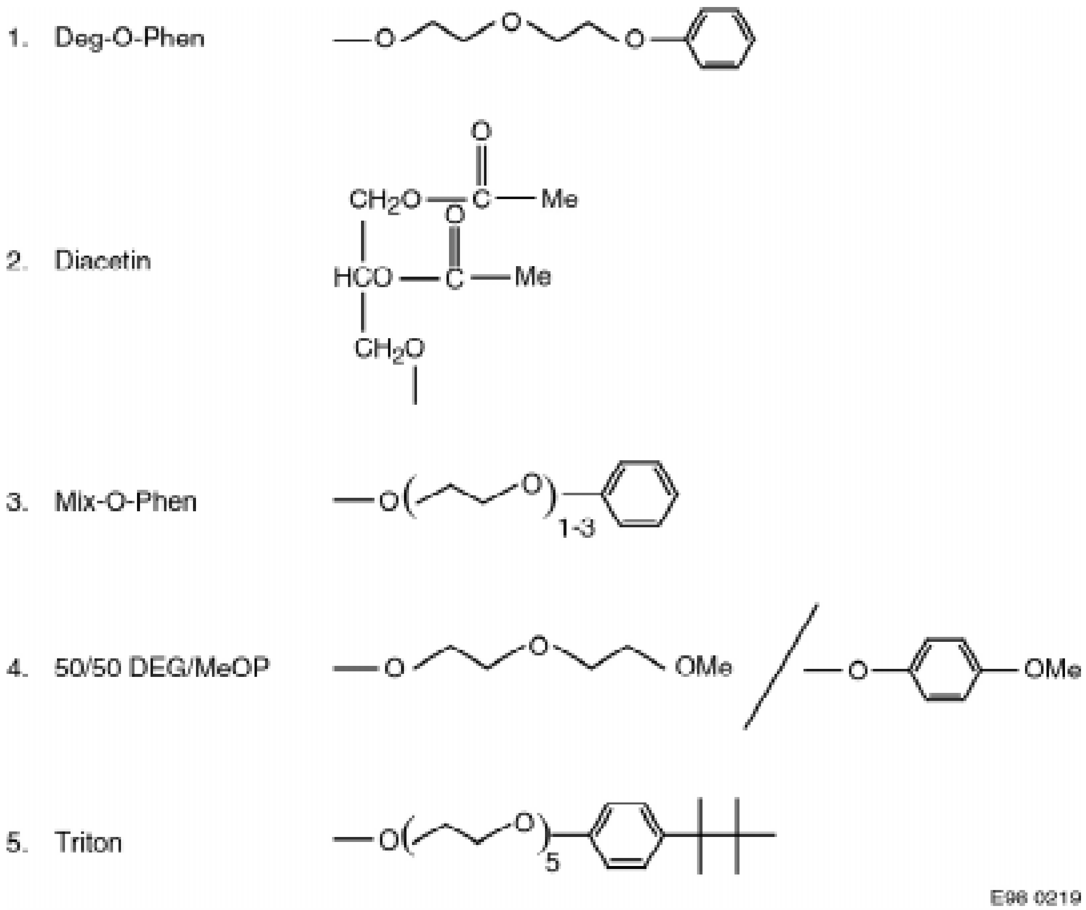

Figure 3. Structures of polymers synthesized for formation of molecular composites.

Table 1. Thermal analysis of Triton molecular composites.

Species	% Ceramic	DSC—T_g (°C)	TGA—Swelling (Δ% Wt. in THF)
Triton-10	10	-35.2	38
Triton-25	25	-33.0	27
Triton-50	50	-35.1	19
Triton (parent)	0	-36.0	Readily dissolved

Table 2. High temperature thermal analysis of a MEEP molecular composite.

40%/60 % MEEP/SiO_2	Experiment #	% Wt. Change 200–300°C	Solvent Wt%
Dry	1	47	N/A
Dry	2	46	N/A
Water Soaked	3	40	98
Water Soaked	4	48	97
THF Soaked	5	44	60
THF Soaked	6	42	59

Table 2 shows the stability of these molecular composites under elevated temperatures and reveals that the swelling due to imbibing of solvents, either organic or aqueous, does not result in decomposition of the composite material.

After the synthesis and basic characterizations of these materials were completed, studies that assess the potential utility to environmental applications have also begun, and these consist of efforts in two primary areas. The first is in the area of metal absorption and transport. Lithium ions have been chosen for the study of basic composite/ion interactions and transport through the matrices. This is meant to provide meaningful data that models interactions of these composite materials with d^0 cations of environmental interest such as cesium and strontium.

The interactions of these composite materials with lithium ions have been studied in three basic ways. The first is by absorption/dissolution studies. Salts of lithium cations have been admixed in solvent swollen gels of the composite materials and the uptake of the salts used as a gauge of the relative affinity of each material for lithium cations. Second, thermal analysis of the composites has been conducted and the difference in the results from a given parent composite in the absence of lithium salts were compared to those obtained from the composite containing the lithium salts. This was used to evaluate specific interactions between the ions and the composite and to give preliminary insight into the possible binding modes between the materials and the ions. Third, lithium transport properties were evaluated using ionic conductivity measurements. AC impedance spectroscopy was used to assess not only the transport of the ions through the bulk matrices, but also to assess the characteristics of the material interface, yielding important information on ion uptake into the composites.

The AC impedance experiments were conducted on polymers and molecular composites that had been complexed with a lithium salt, $LiBF_4$ being one such salt commonly used. The salt was incorporated at a level that corresponds to 24:1 ratio of oxygen carriers to lithium cations.[13] The testing apparatus was placed into a drybox environment to prevent interference with atmospheric moisture and oxygen. The experiments used stainless steel (SS-316) ion blocking electrodes, and were performed on directly cast thin films of the parent polymers to provide a baseline value for lithium mobility through the solid matrix. As this direct casting technique was not compatible with the composite formation techniques, the composites were formed in Teflon dishes and then moved onto the testing electrodes. Due to these experimental constraints, it is difficult to determine if the differing interfacial impedance that was observed was due to a true surface dissimilarity between the composite and the parent polymer, or simply due to the unavoidable variance in experimental procedure. However, the bulk impedance of the composite material was observed to remain the same as in the parent polymer, even for those materials that contained a high percentage of ceramic component. This indicates that while the molecular composites possess enhanced physical properties, their ion transport properties are not adversely affected. Figure 4 shows a typical impedance plot for a molecular composite complexed with lithium salt.

In addition to ion transport, the interaction of these composites with several solvents of interest, particularly water, was also studied. These studies have just been initiated and are being performed in a three-fold approach. First, water uptake is being assessed by swelling and subsequent thermal desorption measurements using thermal analysis equipment. (See Table 2 above for representative data) Second, the material stability to a wide pH regime was assessed by contact soaking experiments followed by repeated mechanical and water uptake analysis, the results being compared to those obtained for the parent polymers. Third, water transport through the composite matrices is being evaluated via pure water pervaporation experiments. These experiments were slated for completion but are yet to be performed due to the shortened timeframe of this year’s efforts.

Subtask B) Organic Passing Polymer Composites. The other strategy employed to address the separations problem was to develop molecular composites designed to selectively pass

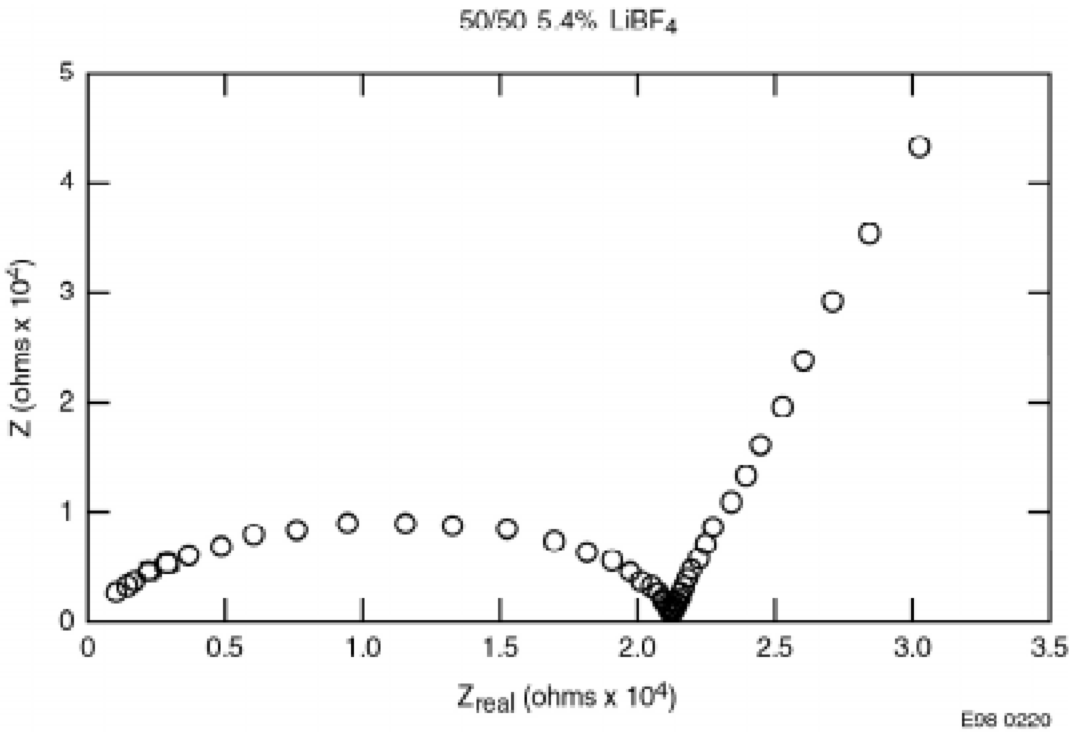

Figure 4. Typical AC impedance spectrum from a molecular composite.

organic liquids and retain both water and metal ions. Polymers identified to perform this task were hydrophobic polymers containing a high aromatic content. A high percentage of this ligand structure possessed a small ether linkage, the methoxy group, to form the potential covalent bonding site with the condensing ceramic component. (vide supra)

As these polymers were not as compatible with the synthetic conditions employed to form the hydrophilic molecular composites, synthesis of these materials proved to be a far more difficult challenge. Solvent substitution for the water/ethanol mixture previously employed was necessary, and it was found that THF/ethanol was an effective replacement. The first parent polymer successfully formed into a hydrophobic molecular composite was the PPXP polymer. The composition of this representative polymer is shown in Figure 5.

Thermal analysis was performed on these new composites and is shown in Table 3. As was observed in the hydrophilic polymers, the intrinsic thermal properties of the parent polymer remained constant as reflected in the unchanged glass transition temperature. Unfortunately, formation of the molecular composite structure did not impart the same degree of structural integrity and enhancement of durability as was observed for the hydrophilic molecular composites. As observed in the TGA experiments, these hydrophobic molecular composites required a much higher level of ceramic component to resist degradation in solvents in which the parent polymer is readily soluble. The reasons for this difference in behavior are not readily apparent at this time, but it is hoped that further experiments designed to elucidate the nature of the bonding in these materials will shed light on this as well.

Two other items of significance have been performed in the execution of this project. First was attendance at four pertinent technical conferences that focused on materials chemistry and state-of-the-art membrane technology and separations science. These were the 10th annual North American Membrane Society Meeting, the 53rd Northwest Regional American Chemical Society Meeting, the 14th

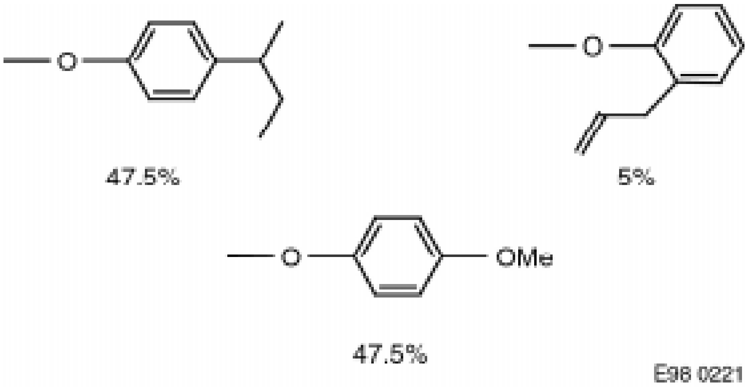

Figure 5. Composition of the polymer PPXP.

Table 3. Thermal analysis of PPXP molecular composites.

Species	Wt% Ceramic	DSC—T_g (°C)	TGA—Swelling (Δ% Wt. in Toluene)
PPXP-10	10	5.1	Dissolved
PPXP-25	25	5.8	Slowly dissolved
PPXP-50	50	5.4	50
PPXP (parent)	0	5.0	Readily dissolved

International Conference on Phosphorous Chemistry, and the 216th National Meeting of the American Chemical Society. Second, a novel procedure to purify the parent polyphosphazenes that improves purity and yield over the existing literature methodology has been developed. The final result of this effort is a manuscript, “Improved Method for the Isolation and Purification of Water-Soluble Polyphosphazenes” to be submitted in 10/98 to the peer-reviewed journal *Chemistry of Materials*.

Part B: Solid Phase Controlled Pore Size Studies.

Library work was conducted to identify phosphazene trimers that have potential for forming solid phase composite materials with a controlled pore size. As there is no precedent in the literature for forming these composite materials, several promising candidate species were identified based on analogy to those polymers that were successfully formed into molecular composites in the preceding section. Similar in nature to the polymer-based molecular composites, trimers containing small ether moieties were chosen as having the most promise. The first of these candidates was synthesized and is shown in Figure 6. Preliminary work in forming molecular composites with this molecule and ceramic precursors was performed by following the synthetic strategy similar to the one known to be successful for polymer composites. The first trimer-based molecular composites that form solid phase materials with a controlled pore size have been synthesized and their physical properties have been determined. The first trimer to form composites is shown below.

The general form of this family of trimers has three parts. First, the phosphazene ring forms the structural basis for the ligands that are attached to each of the phosphorous atoms. These ligands can be comprised of virtually any organic functionality and this offers the tunability desired from these composite materials. Second, the small ether groups at the terminal end of the ligand structure are postulated to form the primary interaction with the ceramic component (*v. s.*). This leads to a method for

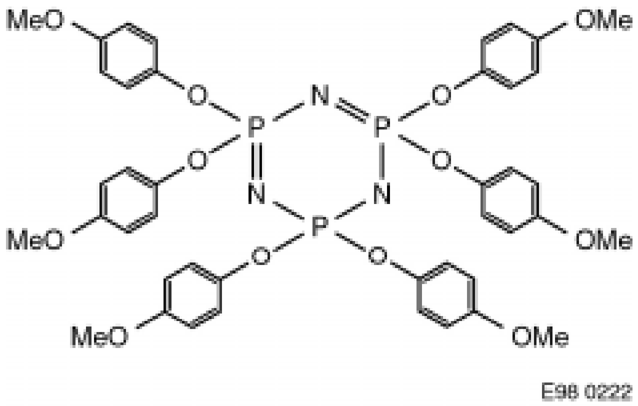

Figure 6. Structure of a representative functionalized trimer ring.

controlling the size of the resultant pore by adjusting the total length of the ligand employed. By varying the size of the group that is bound to the trimer ring, it is expected that the size of the pore formed in the superstructure will be controlled with a high degree of specificity. Third, the internal structure of the ligand possesses multiple sites for further synthetic modification. It is these sites that can be used to introduce functional groups into the interior of the controlled pore. This will impart chemoselectivity into the material enhancing its utility as a separations membrane. Efforts to characterize the structure of these composites and confirm possible bonding modes are currently under investigation. Obtaining a deeper understanding of the interactions between the ceramic and trimer components will allow for generation of new materials that can be custom tailored to meet specific challenges in relevant environmental separations. At this time, these materials still exhibit the brittleness of their all-ceramic analogues, and evaluation of these new materials in model environmental separations is not feasible. Further development of the current synthetic methodologies will afford a greater control over structure-property relationships and is under current investigation.

Summary

During this year, this project initiated research efforts designed to address the EM-relevant problems of separation aqueous organic/metal ion containing mixtures. These efforts centered on the development of hybrid organic/inorganic materials to form durable, effective, and cost-efficient membranes to meet this challenge. Three distinct approaches were employed, designed to form hybrid materials each possessing specific transport properties. The first used hydrophilic polymers as the key component for dewatering and metal ion transport purposes. The second employed hydrophobic polymers for light organic molecule transport. The third used small inorganic ring systems to form solid phase materials with rigorously controlled pore sizes for application as an ultrafilter. The first generation of each of these materials was successfully synthesized and their rudimentary characteristics, both physical and chemical, were determined. Initial ion transport studies were performed, and the data shows that molecular composites exhibit a high degree of promise as materials capable of meeting the challenge of EM-relevant separations in harsh environments. Further separations studies have not been performed to date due to delays in the start of this project (start date was approximately 2/15/98). However, the materials to perform such tests are in place and startup testing will begin in the very near future.

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ADSORPTION AND ABSORPTION MATERIALS FOR MOLECULAR SEPARATIONS

G. A. Moore and E. S. Peterson

Scope and Objectives

Many environmental cleanup challenges exist to which current cleanup strategies cannot technically or cost-effectively be applied. One of the INEEL's primary missions is development of new environmental remediation technologies. Consequently, part of INEEL's FY-98 Core Competency Initiative funding was directed toward developing novel molecular adsorbing/absorbing materials and establishing state-of-the-art materials processing capabilities for such materials. The objective for FY-98 was to establish capabilities for developing compound-specific molecular adsorbents/absorbents. This effort was structured to take full advantage of, and enhance, the materials characterization capabilities at the INEEL's Research Center (IRC).

Contaminants can be removed from a waste or process stream by separation and/or conversion processes. The focus of this effort was developing novel materials that allow separation of EM-focused pollutants from gaseous and liquid sources. Such materials are engineered to have surface sites and/or meso porosity conducive to retaining incident target molecules. Both inorganic and organic materials can be used, e.g., polymer-based ion exchange resins, polyphosphazenes, zeolites, activated oxides, and activated carbon. This project investigated processing mesoporous copper sulfides with a propensity for mercury intercalation from gaseous sources.

The following tasks were established for FY-98:

1. Establish the initial kinetics, structural behavior, and ultimate capacities of the original ore concentrate materials used for mercury sorption that have been developed by the Ukrainians.
2. Establish capabilities for synthesizing high surface area and controlled porosity powders, thin films, and particle coatings.
3. Establish resources and expertise in the area of quantitative powder x-ray diffraction analysis, e.g., phase identification and Rietveld Analysis.
4. Utilize MSI's molecular modeling software, Cerius^2 to understand the mercury intercalation process in copper sulfide materials.
5. Use computational fluid dynamics (CFD) tools to model the top-down spray coating process used for coating particles with adsorbing/absorbing layers.

Technical Accomplishments

Evaluation of Kinetics and Capacities of Naturally Occurring Mineral Sulfides for Mercury Sorption

Several naturally occurring metal sulfide (MS) ores have shown promise as mercury capture materials as documented by scientists in the Ukraine.[1] The mineral phases chosen for these studies at the INEEL are Cu2S (chalcocite), CuS (covellite), MoS2 (molybdenite), and CuFeS2 (chalcopyrite).

Since naturally occurring materials have problems with impurities that make them unsuitable for use in real applications, synthetically pure materials are mandated and were procured for all these experiments. The Cu2S (chalcocite), CuS (covellite), and MoS2 (molybdenite) were all obtained from Aldrich chemical. The CuFeS2 (chalcopyrite) concentrate was obtained from M & W Milling in Virginia City, MT. The chalcopyrite concentrate contains 23.5% of CuFeS2. The Hg, whose source was unknown, was spectrophotometric grade that was on hand and used as is.

An activation process involving a thermal and chemical treatment was applied to the materials to enhance sorption performance. Since that process is proprietary, it will not be discussed here.

Experience suggests that increasing the surface area by generating controlled pore sizes in the materials might enable optimization of mercury sorption.

Four experiments were conducted and are described in the following.

Experiment # 1: 0.3 g of each of the four pure mineral sulfides (MS) were placed in evaporating dishes. The MS were placed on the bottom of a desiccator containing 20g of Hg in an evaporating dish. The desiccator was immersed in a 50^{o}C oil bath. The resulting sample temperature was 42^{o}C on the bottom of the desiccator. Samples were exposed to Hg for 16 weeks.

Experiment # 2: The four MS concentrates were activated by using the proprietary Ukrainian process. 2.5 g of activated MS samples were weighed into evaporating dishes and placed on a stage inside a desiccator containing 40g of Hg in an evaporating dish. The desiccator was immersed in a 50^{o}C oil bath resulting in a 35^{o}C sample temperature. After 5 weeks the temperature inside the desiccator was increased to 42^{o}C. At this point only the covellite was effected by the temperature increase because the other MS samples were at or nearing their apparent saturation points. Samples were exposed to Hg for a total of 14 weeks.

Experiment # 3: The four pure MS samples were placed in evaporating dishes in 7–8 gram quantities and set onto the stage inside a desiccator alongside 40g of Hg also in an evaporating dish. The desiccator was then placed inside of a 68^{o}C oven.

Experiment # 4: The four pure MS were activated by saturating the solids in a concentrated solution of oxalic acid, then filtered and allowed to dry. The MS samples were weighed in evaporating dishes in 7–8 gram quantities and then placed on a stage inside of the desiccator alongside 40g of Hg. The desiccator was put into a 68^{o}C oven.

Powder X-ray diffraction (XRD) patterns were performed on a XDS2000 Scintag XRD spectrometer with a solid state detector.

Results of Experiment 1: Table 1 below shows the mass change that occurred over time for the four pure MS samples. The masses reported are running cumulative totals in milligrams. Only the covellite sample absorbed any significant amount of Hg. Over the entire 16 weeks the covellite absorbed a total of 114.7 mg of Hg giving a solids concentration of 27.5 wt% of Hg. Figure 1 correlates the total number of days to the cumulative wt% of Hg addition to the chalcocite and chalcopyrite samples. Figure 2 shows the total number of days to the cumulative wt% of Hg for the covellite.

The slope of these plots gives the rate of Hg incorporation. For the chalcocite and chalcopyrite the rate of Hg incorporation is 0.0104 wt% day^{-1} and 0.0141 wt% day^{-1} respectively. The rate for the covellite sample is 0.225 wt% day.$^{-1}$

Table 1. Shows the cumulative mass increase in milligrams and the respective concentration in wt% of Hg for the pure samples of the mineral sulfides exposed to Hg vapor in experiment # 1. The initial sample masses were 300mg. $T = 42^{o}C$.

Day	Chalcocite (mg)	Chalcocite wt% Hg	Covellite (mg)	Covellite wt% Hg	Molybdenite (mg)	Chalcopyrite (mg)	Chalcopyrite wt% Hg
10	2.8	0.9	7	2.2	0	6.2	2
18	2.9	0.93	17	5.2	0	7.2	2.3
24	2.9	0.93	23.1	7.1	0	7.5	2.4
35	3.5	1.1	34.3	10.0	0	7.5	2.4
52	3.6	1.2	45.3	12.9	0	7.8	2.5
66	4	1.3	55.4	15.5	0	9.3	3
80	5.3	1.7	71.3	19.1	0	9.3	3
88	5.3	1.7	78.4	20.6	0	9.3	3
97	5.3	1.8	86.6	22.3	0	9.3	3
115	5.3	1.7	114.7	27.5	0	9.3	3

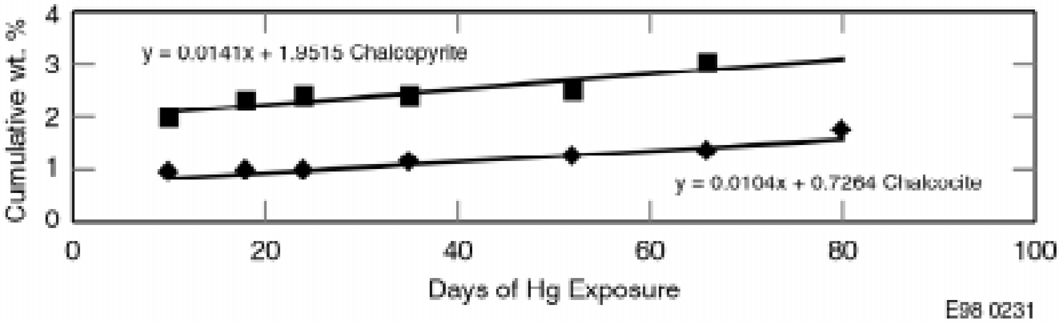


Figure 1. Rate of Hg incorporation into a pure sample of chalcocite and chalcopyrite. Total sample mass was 0.3065 g and 0.3014 g respectively.

Another observation made for covellite in experiment 1 was a change of color. The exact point of the color change is unknown; however, the covellite turned from the familiar blue of Cu(II) complexes to a gray similar to that of the Cu(I) chalcocite. This suggests the possibility of redox chemistry occurring between the Hg and the covellites

Both the chalcocite and chalcopyrite concentrate did adsorb a small amounts of Hg but the molybdenite absorbed none. Both of the chalcocite and chalcopyrite samples show a Hg saturation point. For chalcocite, this occurred after 66 days with a Hg concentration level of 1.7 wt%. The chalcopyrite saturation point was reached after 52 days at 3.0 wt% of Hg. The chalcopyrite has a slightly higher threshold for Hg incorporation than the chalcocite. This is even more significant considering the chalcopyrite concentrate sample contains only 24% of $CuFeS_2$ with the remaining makeup of the sample consisting of various gangue materials. The covellite saturation point has not yet been reached.

Results of Experiment 2: Because of differing sample masses and experimental temperature, a direct comparison of experiment # 2 (activated samples) and experiment # 1 (pure samples) must be done with caution. Comparing the concentration of the Hg incorporated into the MS normalizes the two experiments with each other.

The activated chalcocite sample absorbed 4 wt% of Hg until saturation. The activated chalcocite shows a greater ability to incorporate Hg than the pure form. This result may be significant considering the lower temperature in experiment # 2. The rate of Hg incorporation has also gone up by nearly a factor of eight. The chalcopyrite concentrate also behaved in a similar fashion with a saturation level of 2 wt% of Hg. This is a smaller saturation level than the pure form counterpart in experiment # 1 and can be speculative because of the lower temperature. The chalcopyrite has a smaller saturation point for the activated phase but the rate of incorporation was greater by a factor of five than the pure form. This suggests the activation process effects the chalcopyrite's ability to incorporate Hg. Like the pure form of molybdenite, the activated form did not absorb Hg. Table 2 shows the cumulative total mass changes for three of the activated mineral sulfides with time Hg. The plot for the chalcopyrite results in a rate of 0.0523 wt% per day. Figure 2 shows the incorporation of Hg and gives the resulting rate of Hg incorporation for chalcocite as 0.0846 wt% day^{-1} up to the point of saturation. Table 3 shows the magnitude of mass change of the activated MS covellite. The total number of days of Hg exposure vs. the cumulative wt% is plotted in Figure 3. The slope of this graph gives the rate of Hg incorporation as 0.351 wt% day^{-1}. The activated covellite has about a 33% greater rate of Hg incorporation than the pure form of the covellite shown in Figure 1.

Table 2. Cumulative mass changes for activated mineral sulfides at 35°C.

Day	Chalcocite		Molybdenite	Chalcopyrite	
	Total mg	Wt.%		Total mg	Wt.%
7	17.9	0.7	0	2.5	0.1
24	52.5	2.1	0	33.7	1.3
38	84.3	3.3	0	44.5	1.7
46	100.6	4.0	0	46.4	1.8
52	100.6	4.0	0	46.4	1.8

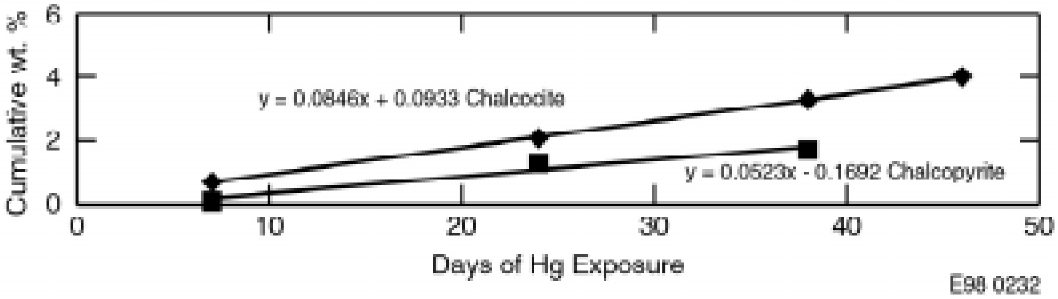


Figure 2. Rate of Hg incorporation into the activated samples of chalcocite and chalcopyrite. Total sample mass was initially 2.5 g.

Table 3. Mass change of activated covellite with exposure to Hg vapor. Mass increases are in milligrams and the Total mass is in grams. T = 42°C

Days	Mass Increase	Total Mass Increase	Total Mass	Wt% of Hg
8	108.8	108.8	2.637	4.1
14	144.5	248.8	2.7775	9
22	108.1	356.9	2.8856	12.4
31	105.2	462.1	2.9908	15.5
49	178.3	640.4	3.1691	20.2
52	54.1	694.5	3.2231	21.5
61	132.4	793.2	3.2707	24.3

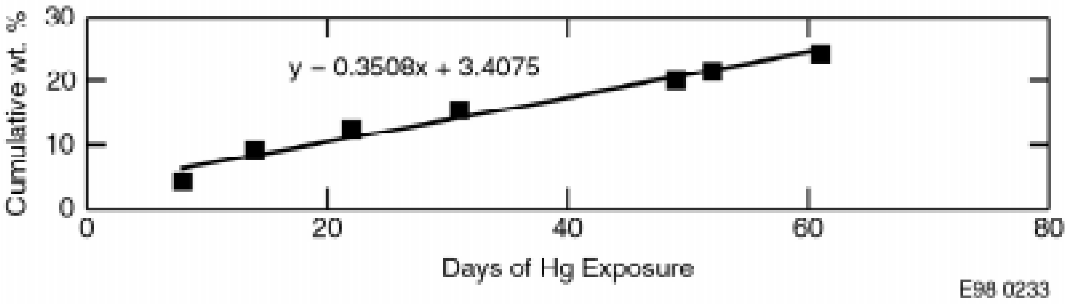


Figure 3. Rate of Hg incorporation into an activated sample of covellite. Total sample mass was initially 2.5 g.

The rate of Hg incorporation by covellite is not only faster than chalcocite and chalcopyrite, but its capacity is larger since the saturation point has to-date not been reached. After five weeks of exposure to Hg, the temperature inside the vessel containing the activated samples was increased by 7°C to a final temperature of 42°C. This resulted in an increase of Hg absorption. The increased rate of Hg consumption occurred only for the covellite sample because the chalcocite and chalcopyrite were at or near their saturation points. The data presented here for covellite is for incorporation of Hg after the temperature was increased in experiment # 2.

Table 4 gives a comparison for the Hg incorporating abilities of the MS studied in experiments # 1 and # 2. The molybdenite is not shown since it did not absorb any Hg. The comparison of the activated and pure forms of chalcocite and chalcopyrite are shown for the Hg concentration at their saturation point.

Powder X-Ray Diffraction Data for Experiments # 1 and # 2: The powder X-Ray Diffraction (XRD) patterns were obtained for both the activated and pure samples of the covellite. Upon incorporation of Hg, both covellite phases show changes in their respective diffraction patterns. Data were taken for the unactivated and activated materials containing 12.9 wt % of Hg and 22.3 wt% of Hg respectively. Reflections at $2\theta = 26^{o}C$ and $2\theta = 31^{o}C$ are new reflections in the covellite powder pattern. While the reflections at $2\theta = 32^{o}$ and $2\theta = 33^{o}$ nearly disappear with increasing Hg concentration.

The same changes in the XRD powder patterns are seen in the patterns of the activated covellite from experiment # 2. Like experiment # 1 there are new reflections at $2\theta = 26^{o}$ and $2\theta = 31^{o}$ upon exposure to Hg. Also the $2\theta = 48^{o}$, 32^{o}, and 33^{o} all lose intensity upon greater incorporation of Hg. Peak

Table 4. Comparison of the total wt% of Hg for both the activated and pure forms in experiments # 1 and # 2.

Chalcocite		Chalcopyrite		Covellite	
Activated 35°C	Pure 42°C	Activated 35°C	Pure 42°C	Activated 42°C	Pure 42°C
4 wt%	2 wt %	1.8 wt%	3 wt%	24.3 wt% in 61 days	15 wt% in 66 days

heights cannot be compared directly for the patterns because they are not quantitated. None of the new powder patterns have been indexed.

The powder patterns shown in Appendices A and B indicate that nothing is structurally different between the activated and pure covellite after exposure of Hg. This suggests that the two phases incorporate Hg in the same manner. The activated sample simply incorporates Hg at a greater rate. This is best seen by comparing the activated and pure phases where they have about 15 wt% of Hg incorporated into them. The powder patterns appear nearly identical.

If one compares the pure covellite, activated covellite and Hg exposed covellite from experiment # 2. This series of powder patterns suggest that the activation process is not effecting the molecular structure of the MS.

The XRD powder patterns of the different phases of chalcocite and chalcopyrite show very little change upon incorporation of Hg. With the small quantities present at the saturation levels this is not surprising. At the saturation point for chalcocite the only change in the powder pattern is broadening around $2\theta = 27^o$ and a shifting of the strong reflection at $2\theta = 47.5^o$. There is no evidence in the case of the chalcopyrite for structural changes upon Hg incorporation, however one difference between the powder patterns is a broad, low intensity reflection at $2\theta = 31^o$.

Results of Experiments # 3 and # 4: The final two experiments will not be discussed in much detail because they have been monitored for only two weeks to date.

Although it is only 14 days old, this experiment is giving drastic differences in wt% incorporation of Hg because of the higher temperature used. Since the temperature is uniform, as are sample masses, this makes direct comparison between pure and activated phases possible. Mass change measurements have only been completed once for this set of experiments, yet they still give some indication of what is happening. In the tables below the molybdenite has been left out due to the lack of any Hg incorporation into it. Table 5 shows the wt% of Hg incorporated into pure phases of the mineral sulfides after 14 days of exposure to Hg at 68°C.

Table 6 below shows the mass change data of Hg incorporation for the activated MS in experiment # 4.

Some preliminary comparisons between experiments # 3 and # 4 compare well with experiments # 1 and # 2. The greater increase in Hg incorporation is, of course, expected with the higher temperatures. The qualitative behavior of the MS is comparative in that all four experiments the chalcocite shows a greater ability to incorporate Hg in the activated phase compared to the pure phase. Conversely, the chalcopyrite shows a diminished ability for incorporation of Hg in the activated phase compared with its pure phase. The greater Hg incorporating ability of the activated covellite is magnified at 68°C compared with 42°C. At 68°C the covellite had incorporated 20.2 wt% of Hg in only 14 days. The activated sample at 42°C took 49 days to incorporate this quantity of Hg.

Table 5. Mass change for Hg incorporation for pure phases of the listed mineral sulfides at 68°C.

Sample	Days	Mass Increase (g)	Initial Mass (g)	Total Mass (g)	Wt.% Hg
Chalcocite	14	0.0568	7.2343	7.2911	0.7
Chalcopyrite	14	0.1534	7.2721	7.4255	2.1
Covellite	14	0.2471	7.0835	7.3306	3.4

Table 6. Mass change for Hg Incorporation for activated phases of the listed mineral sulfides at 68°C.

Sample	Days	Mass Increase (g)	Initial Mass (g)	Total Mass (g)	Wt.% Hg
Chalcocite	14	0.1058	7.3923	7.4987	1.4
Chalcopyrite	14	0.129	8.2781	8.4071	1.5
Covellite	14	1.8791	7.1918	9.0709	20.2

Visual inspection revealed the greater incorporation of Hg in activated covellite compared to the pure form. In both phases, the surface color of the covellite went from blue to gray but only the surface of the pure form was gray. The activated covellite was gray nearly all the way through the entire 2 mm thickness of the sample.

Synthesis of Metal Sulfides

Ukrainian scientists have intercalated mercury in copper sulfides over the past several years, however, a comprehensive understanding of the intercalation mechanism and stability of the resulting compounds has yet to be attained. There are several methods for synthetic production of metal sulfide powders.[2,3] One approach for enhancing the mercury vapor uptake via synthesis of high surface area copper sulfide powders has been investigated. The synthesis route being used for these studies is based on work reported by Mart T. Anderson et. al.[4] The actual synthesis procedure used by INEEL researchers is as follows:

- Prepare a surfactant solution by mixing water, ethanol, and the surfactant hexadecyltrimethylammonium bromide (CTAB) at 80°C. A 1.4/0.5/0.2 mole ratio was used. This surfactant solution is used to control the porosity/surface area of the sulfide precipitate. For comparison, material was also made without the using CTAB.

- After obtaining a clear surfactant solution, 0.03 moles of Na2S was added and allowed to dissolve.

- Prepare an aqueous copper chloride solution by dissolving 0.03 moles of CuCl2 in 1.4 moles water.

- In a drop-wise fashion, add copper chloride solution to stirring surfactant/sodium sulfide solution (forming a copper sulfide precipitate).

- Recover precipitate via aqueous washing using Millipore pressure filtration apparatus.

- Dry the washed precipitate at 110ºC for several hours.

- Calcine precipitate in 4% H_2S/Ar at 200–450°C.

Precipitates with and without CTAB showed crystalline character as established using x-ray diffraction (XRD)analysis on powder samples. Both precipitates contained a mixture of CuS, Cu_9S_8 and $CuSO_4(5H_2O)$, as well as one or more unidentified secondary phases. The CTAB surfactant was found to have a dramatic effect on the precalcined particle size (Figures 4 and 5). The discrete precipitate particles were ~0.05–0.1 µm when CTAB was used and >10 µm in its absence—a 100–200 times difference. XRD results indicate that when calcination temperatures of 300–450°C are used, Cu_2S and $Cu_{1.96}S$ remain and the hydrated sulfate phase is eliminated. Ongoing experiments are focused on obtaining the CuS "covellite" phase and, alternatively, using copper nitrate precursors. At this time, the mesoporous nature of the calcined copper sulfide samples has not been established. This will be accomplished using BET surface area analysis techniques incorporating gaseous monolayer adsorption and desorption.

Characterization of CuS and Mercury Intercalated CuS Structures

This activity was in support of a collaborative effort on the part of Montana State University (MSU). Their task being the controlled exposure of copper, copper/iron, and molybdenum sulfides to mercury vapor and characterization of the structural changes occurring at the molecular level via XRD. Based on mercury intercalation in titanium and tantalum disulfides,[5,6] it is expected that the C-axis of the CuS's hexagonal unit cell will significantly expand with intercalation of mercury into the interstitial sulfur planes.[7] In order to quantify the structural modifications resulting from mercury intercalation in covellite, INEEL researchers initiated a molecular modeling task. With MSI's Cerius^2 software, it was possible to

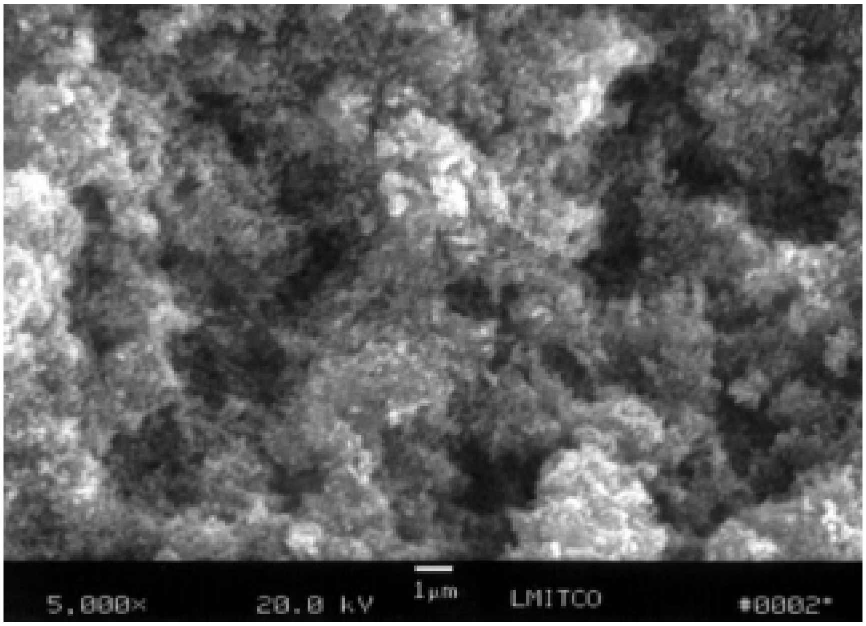


Figure 4. Copper sulfide precipitate prepared using CTAB surfactant.

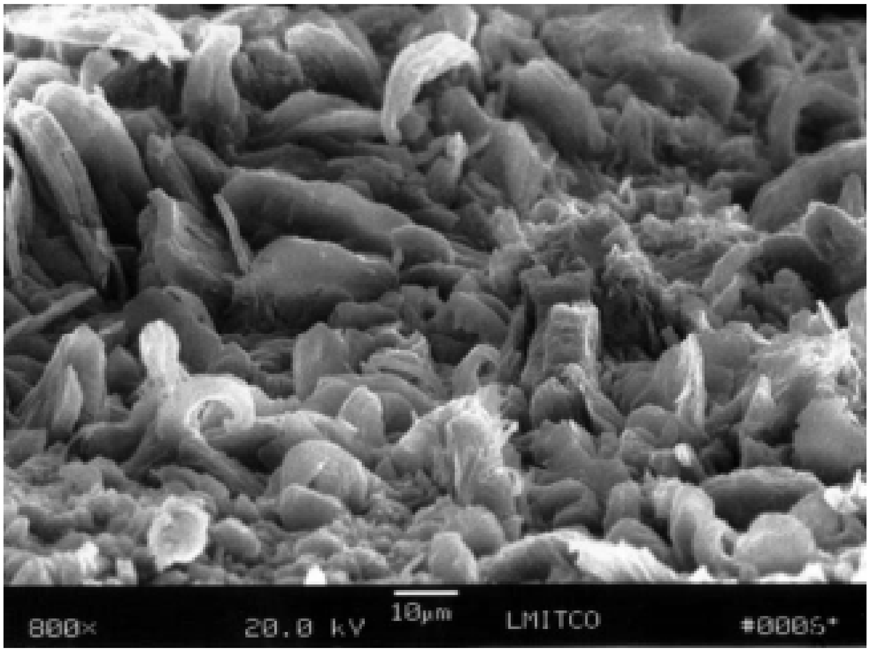


Figure 5. Copper sulfide precipitate made without CTAB surfactant.

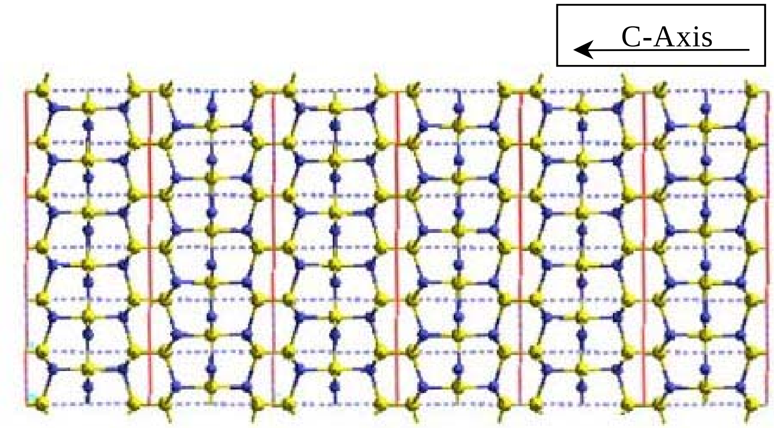
construct a molecular model of the covellite structure, Figure 6-A, and predict the material's XRD powder pattern (Figure 7). This exercise confirmed the single-phase nature of the CuS used by MSU in their intercalation experiments.

Next, the XRD powder pattern for a 30 wt% mercury containing covellite sample was compared with the original CuS structure, Figure 8. The data indicate that a very significant structural change occurred with mercury vapor exposure. The degree of structural modification is beyond the range that Rietveld structural refinement can be directly applied. INEEL researchers are currently using the superlattice features of Cerius^2 in order to generate a hybrid covellite model that allow the sulfur planes to be discretely separated while maintaining the dimensional integrity of the Cu-S polyhedral. Mercury atoms can be inserted into the hexagonal sulfur planes as illustrated in Figure 6-B and the XRD powder pattern calculated.

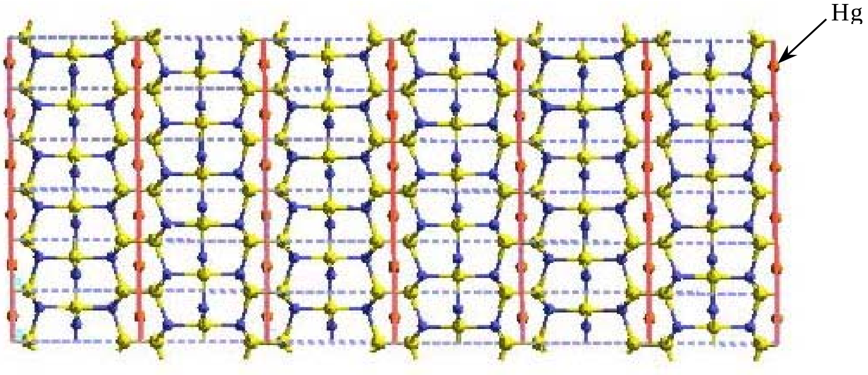
Enhanced Materials Processing Capabilities

In order to effectively utilize high surface area/controlled porosity materials in separation processes, it is desirable maximize the interaction of the target pollutant. This can be accomplished by fabrication of bulk porous material, supported membranes, infiltrated media, and coated media. During FY-98, the following processing equipment and characterization instruments were configured in preparation for future adsorbent/absorbent media preparation.

Controlled Atmosphere Calcining Station. The calcining station (Figure 9) consists of a programmable 1,700°C Lindberg tube furnace, a two cylinder gas cabinet, a mass flow controlled, a vacuum pump, a vented enclosure with acrylic walls/doors, and a hydrogen sulfide monitor. To date, it has been used to thermally treat, in 4% H2S/Ar, copper sulfide precipitate samples.



A. CuS "Covellite" Hexagonal Structure



B. Covellite with Hg Atoms Placed in 002 Interstices

Figure 6. Molecular structure of CuS covellite. A: pure state and B: a hypothetical representation of complete mercury intercalation resulting in expansion of the C-axis.

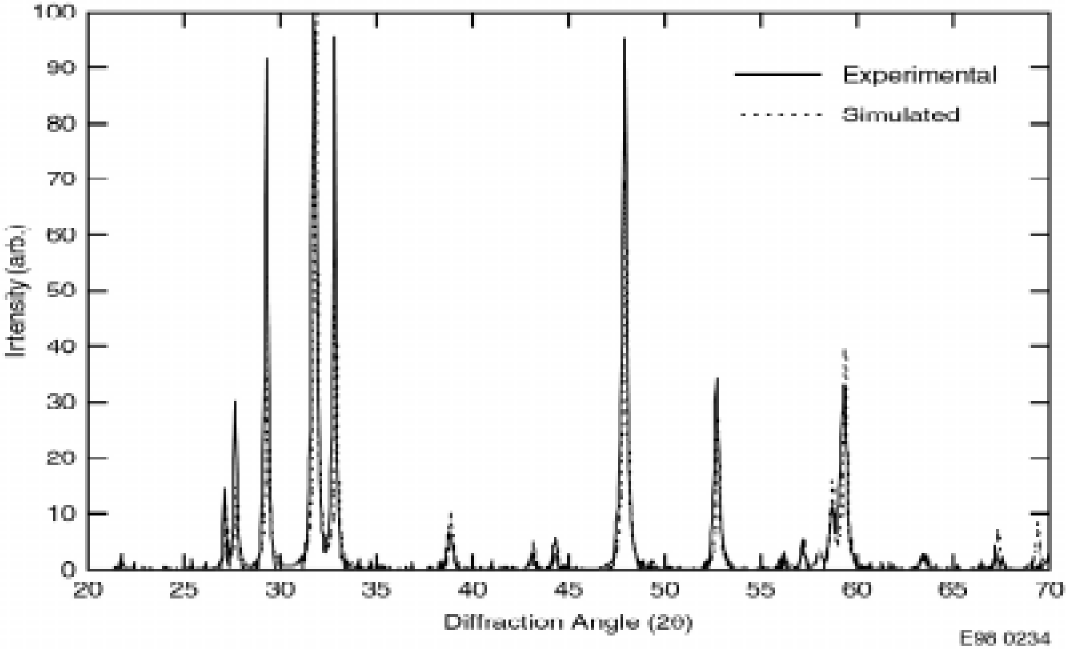


Figure 7. Graph showing experimental and calculated XRD powder pattern of pure covellite.

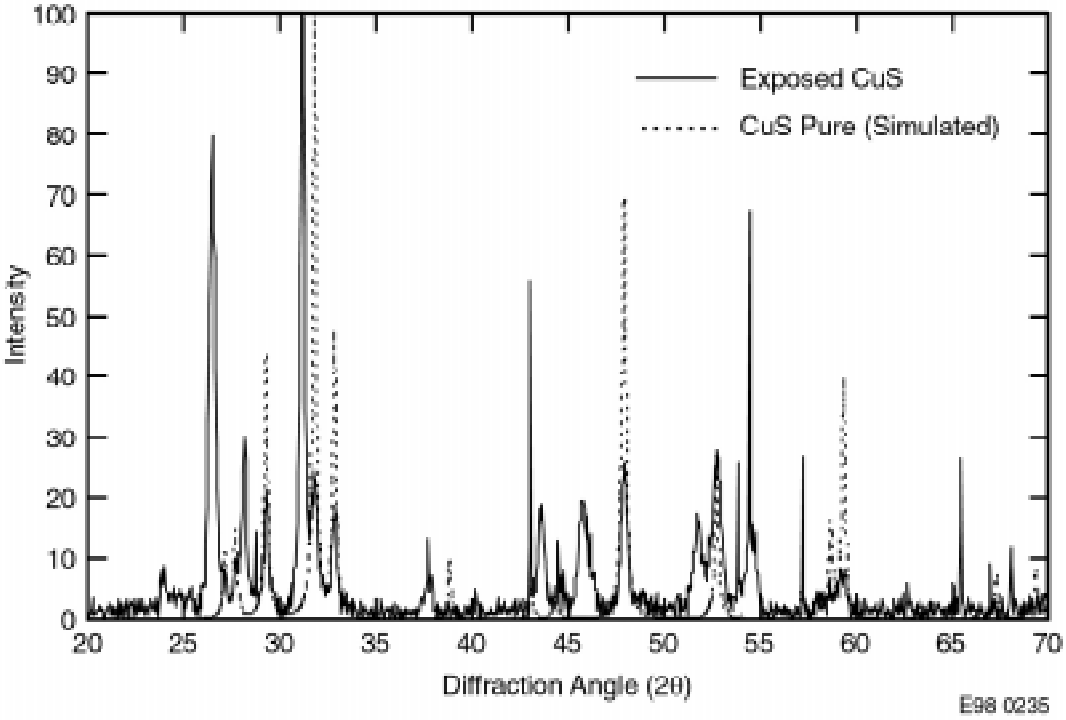


Figure 8. Graph showing XRD powder pattern of pure and mercury exposed covellite.

Figure 9. Controlled atmosphere calcining station.

Programmable Spin Coater. For spin casting controlled thickness/structure films, a speed/acceleration programmable casting maker (see Figure 10) was procured (Roto-Film^{TM} Rotational-Casting Film Maker from International Crystal Laboratories). The unit has parabolic and flat casting platens, a 500–5,000 rpm spin range, a programmable PID motion controller, and hold six resident casting cycle profiles. The caster will be used for making controlled thickness/structure thin films for subsequent characterized via FTIR, x-ray diffraction, surface area analysis, and adsorption/absorption analysis. To date, the Roto-Film rotational caster has been used for casting polyphosphazene films on glass substrates.

Thin Film Measurement Instrument. For measuring thickness and surface roughness of cast films/coating, a Filmetrics F20 Thin-Film Measurement System was procured (see Figure 11). The F20 measures transparent or translucent films from 30 Å to 50 µm thick via spectral reflectance. Spectral reflectance measures the amount of light reflected from a thin film over a range of wavelengths, with the incident light normal (perpendicular) to the sample surface. Typical accuracy is within 10 Å.

Figure 10. Photo of Roto-Film^{TM} rotational-casting filmmaker.

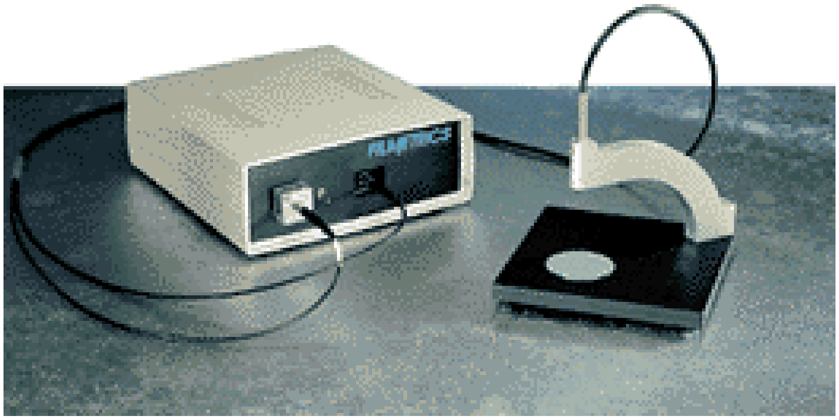


Figure 11. Filmetrics thin-film thickness measurement instrument.

Top-Down Spray Coated. For processing of thin adsorbing/absorbing coatings on particulate/bead media, a Uni-Glatt^{TM} spray coater/spray drier, purchased in 1997 with general purpose capital equipment (GPCE) funds, was set up in the ceramics laboratory at the IRC (see Figure 12). Spray drying is one of many techniques for applying a coating to a substrate. It is widely used in process industries to produce various chemicals, food products, detergents, cosmetics, and pharmaceuticals. The requirement for a coating may be to improve the taste of the product, improve its shelf life, improve its appearance, simplify packaging, modify drug release rate, etc. The process involves placing the desired coating substance in solution or suspension, atomizing this suspension, and forcing the droplets to impinge and wet the substrate, and subsequent drying and adhesion of the film on the substrate. At the heart of this process is the generation of coating droplets. Atomization performance directly affects drying time and energy as well as final product quality.

One of the critical components of the Glatt spray-drying unit is the atomizing spray nozzle. The ideal atomizer for film coating application processes would produce droplet size spectra of low mean diameter (20–30 μm), handle a range of low-viscosity suspensions, be of simple construction, and have simple controls for changing spray angle. Two basic types are available—airless and pneumatic nozzles. The nozzle used in the Uni-Glatt is pneumatic.

The nozzle has separate inlets for water and air, and an adjustable air cap. The air cap position is adjusted by threading it in or out and tightening it against the air cap lock nut. This adjustment determines the width of the gap between the liquid insert and the air cap, thereby affecting the airflow rate and velocity for a specified air pressure. Other variables affecting the performance of this pneumatic nozzle include solution viscosity, density, surface tension, liquid flow rate, and flight distance/angle from nozzle to substrate. Correlations are available for predicting the droplet size distribution produced by a nozzle. However, these correlations are very dependent upon the specific details of the nozzle design. Therefore, in order to characterize the Glatt spray nozzle and to provide basic spray information for concurrent modeling efforts, drop size distributions were measured experimentally for a variety of air pressures, liquid flow rates, and nozzle configurations.

In order to perform the spray nozzle characterization studies, the Glatt nozzle was mounted in an existing droplet size distribution measurement facility located at the May Street North Laboratory. This facility consists of a two-component laser-based phase Doppler particle analyzer (PDPA), spray booth, water and air delivery systems, high-speed photographic equipment, and laser sheet lighting. The facility is referenced[8] in detail by McCreery. Dry air and deionized water were used for the spray. High-speed photographs using both strobes and laser sheet lighting were obtained of the spray for a variety of flow

Figure 12. Uni-Glatt spray coater/spray drier.

conditions. A representative photograph is presented in Figure 13. Spray angle and spatial inhomogeneities of the droplet size can be discerned from these images. A particular concern was the presence of some very large droplets, suggesting that a significant percentage of the spray mass flux could be contained in a small number of large droplets. These large drops could present a problem when trying to obtain very uniform spray coatings. One of the objectives of the spray characterization work was to identify nozzle operating conditions that would produce more uniform sprays.

Detailed PDPA measurements were obtained for a water spray under a range of airflow pressures, water flow rates, and air cap positions. The experimental test matrix is presented in Table 7. All measurements were obtained at an axial distance of 3 inches downstream from the nozzle exit. For each flow condition, spray data were obtained at several radial positions in 0.25-inch increments from R = 0 to R = 1.0 – 1.5 inch. The PDPA measurements include axial and radial droplet velocities, drop size distributions, and spray volume flux. In addition, drop size to velocity correlations can be extracted.

Results of the spray characterization measurements including size/velocity cross correlations have been saved on the data acquisition computer. Some of the results have also been transferred to a spreadsheet for further analysis and plotting. Representative plots of mean data are presented in Figures 14 and 15. In each of these figures, trends of arithmetic mean diameter, volume mean diameter, axial velocity, radial velocity, and volume flux are plotted with respect to radius. The mean droplet

Figure 13. Photograph of Glatt pneumatic spray nozzle.

Table 7. Test matrix for spray nozzle characterization.

Air Pressure (psig)	Air Cap Position (# turns)	Water Flow Rate (l/min)
20	0.33	79.5
20	0.67	79.5
20	1.00	79.5
20	0.33	132.5
20	0.67	132.5
20	1.00	132.5
20	2.00	132.5
15	0.33	79.5
15	0.67	79.5
15	1.00	79.5
20	3.00	79.5
30	3.00	53.0

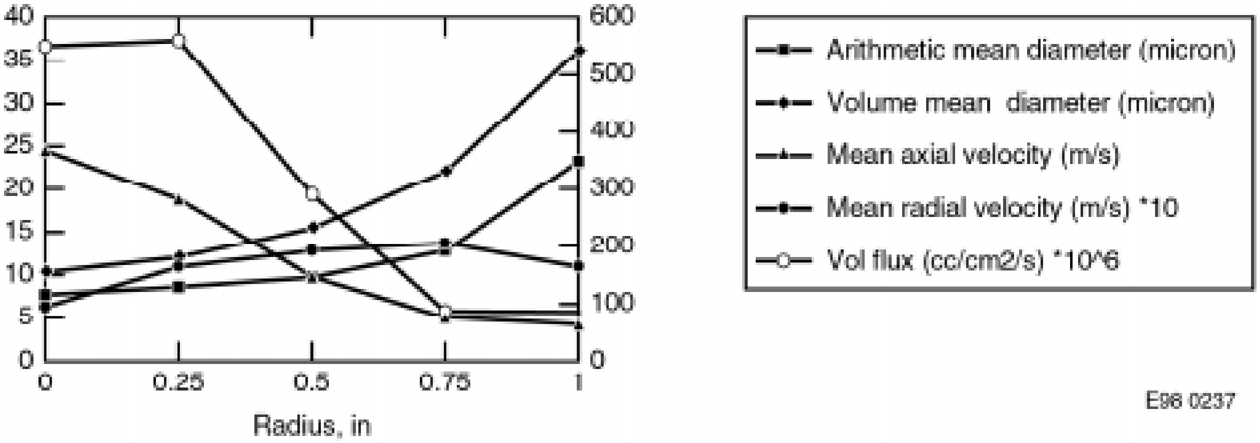


Figure 14. Spray data for 79.5 ml/min water flow rate, 20 psig air pressure, and 3-turn air cap position.

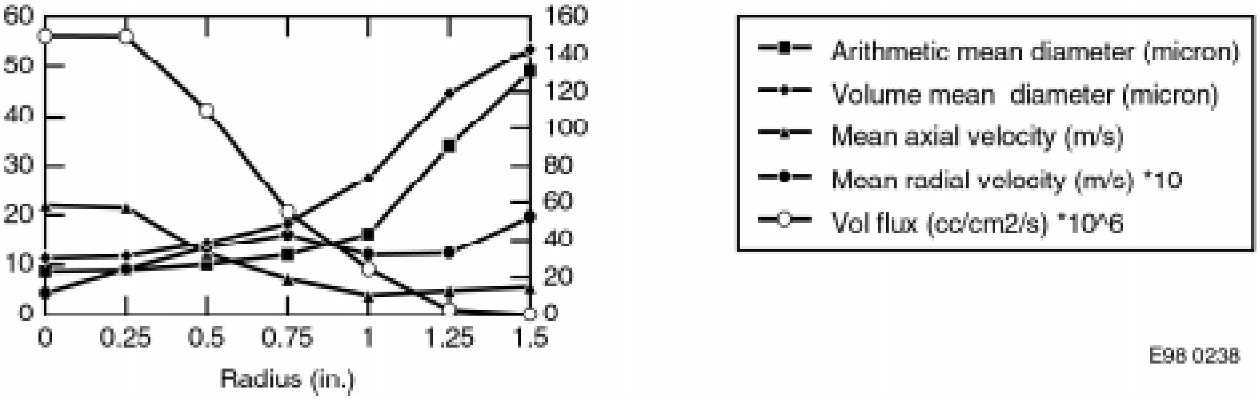


Figure 15. Spray data for 79.5 ml/min water flow rate, 20 psig air pressure, and 3-turn air cap position.

diameters trend upward with increasing radial distance from the spray centerline, indicating that the larger drops tend to be concentrated in the outer spray region. Axial drop velocities are largest near the centerline. Radial drop velocities are near zero on the spray centerline and increase slightly with radius. Volume flux values are generally highest near the spray centerline, despite the larger droplet sizes observed at larger radii. It should be noted that the integrated volume flux values are lower than the known total volume flux. The PDPA misses a few of the large drops (100 µm or greater). Each 100 µm drop contains as much volume of water as 1,000 10-µm drops, so missing even an occasional large drop results in large errors. Therefore, the volume flux values should be interpreted in relative terms only.

The smallest and most uniform droplets were produced with the highest air pressures, lowest water flow rates, and furthest-out air cap position (i.e., 3 turns). These conditions were met for the data presented in Figure 16. Note that the mean droplet diameters were relatively uniform from the centerline to the outer spray region for these conditions.

A typical drop size distribution is presented in Figure 17 for the same operating conditions as the mean data presented in Figure 14. For these operating conditions, the arithmetic mean diameter at a radial position of 0.25 inches from the spray centerline was 8.9 µm. Large number counts of droplets were observed over the range from 1 µm to 30 µm, however. This type of distribution was fairly typical.

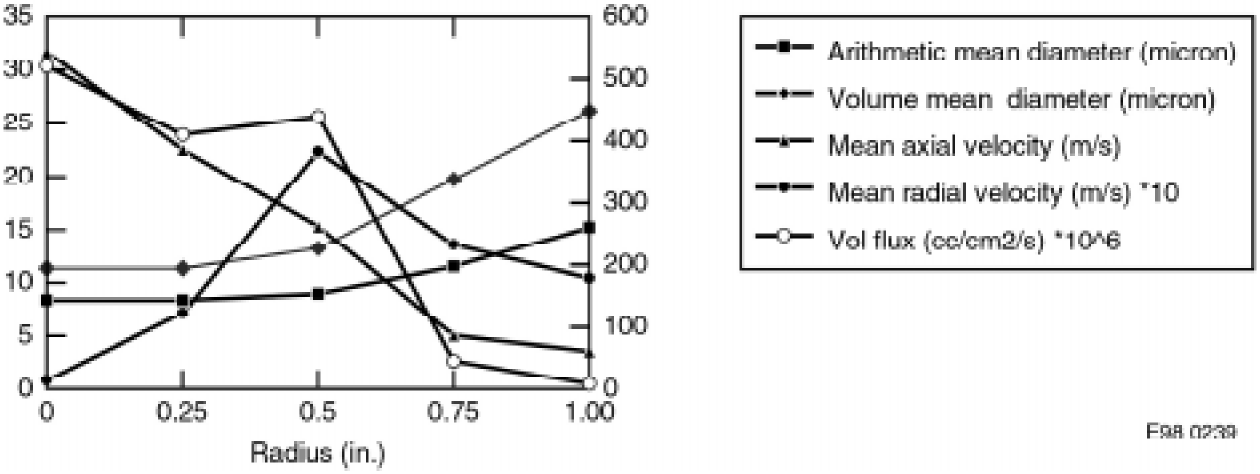


Figure 16. Spray data for 53 ml/min water flow rate, 30 psig air pressure, and 3-turn air cap position.

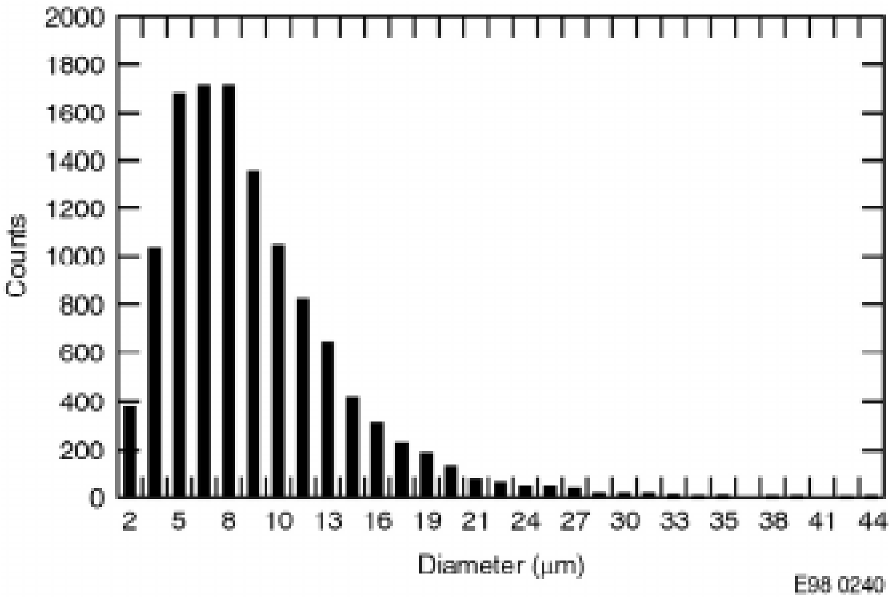


Figure 17. Droplet size distribution histogram; 79.5 ml/min water flow, 20 psig air pressure, 1-turn air cap position, R = 0.25 in.

The Uni-Glatt particle spray-coating unit has been fully prepared for testing various techniques for producing porous coatings. The atomizing spray nozzle has been fully characterized in terms of expected drop sizes and how these drop sizes are affected by airflow pressure, liquid flow rate, and nozzle configuration.

Modeling of the Top-Down Spray Coating Process

Given the large number of processing parameters controlling the deposition rate and morphology of the coating process, a computation fluid dynamics (CFD) modeling effort was initiated with the objective of developing a useful simulation/optimization tool. The 3-D multiphase model being developed will incorporate three phases (gas, liquid, and particles “solid”), the porous baffle plate, the porous exist filter, the dynamics of the pneumatic spray nozzle, and the evaporative coating process.

For this challenging task, CFDLIB, a library of computer codes being developed at Los Alamos National Laboratory was selected. CFDLIB is capable of solving a wide variety of CFD problems in two- and three-space dimensions, was selected. The codes are related to one another by virtue of a set of common features. These include the use of a finite-volume computational scheme in which all state variables are cell-centered, a multiblock data structure that enables highly efficient processing on modern supercomputers, and an arbitrary Lagrangian-Eulerian (ALE) split computational cycle.

All flow speed regimes are accessible in the library, ranging from fully incompressible to hypersonic. Code volumes exist that enable multifluid and multiphase computations with an arbitrary number of fluid fields, each with their own set of conservation equations. The design of each code volume in the library is modular, making the development of codes for specialized applications exceptionally fast. A current area of application of CFDLIB is the modeling of complex reactive flows in multiphase, multifield problems; such is the focus of our work.

To date, 2-D single-phase simulations have been performed. Namely, simulation of the particle's entraining air and the counter impinging nozzle gas in the coating chamber, Figure 18. Two significant model development tasks are: (1) incorporation of the porous baffle plate, the exit filter, the solid phase "glass beads," a liquid phase "coating solutions," and (2) introduction of the thermal source "heater" and the evaporating liquid/solid "coating" dynamics. Due to the complexity of the problem, a parallel version CFDLIB will be utilized in conjunction with a high-end multiprocessor workstation. It is hoped that through simulation of the coating process we will be able to precisely control coating thickness and morphology; thus optimizing the adsorbing/absorbing functionality of materials systems under consideration.

Summary

Our FY-98 effort was initiated in February of 1998. Due to personnel shortages we did not effectively begin to work until early April. Two concurrent foci were pursued: (1) processing of adsorbent/absorbent materials and (2) enhancement of the INEEL's materials processing core base. The processing activities were devoted to aqueous processing of high surface area copper sulfide powders. To date, submicron copper sulfide powders have been synthesized and characterized using XRD, SEM, Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA).

The four mineral phase sulfides, chalcocite (Cu_2S), covellite (CuS), molybdenite (MoS_2) and chalcopyrite ($CuFeS_2$) were tested to determine their feasibility to absorb Hg vapor. The mineral sulfides were exposed to the Hg in two forms. The pure form is the mineral sulfide exposed directly to Hg vapors as solid powders. The activated form is thermally and chemically treated using a proprietary process, then exposed to the Hg vapor as powders. Covellite proved to be the most effective Hg absorber of the four mineral sulfides. The activated form of the covellite was a better absorber than the pure form. Chalcocite and chalcopyrite did have some Hg absorbing qualities but they were not as effective as the covellite. Activation did not significantly improve the Hg absorbing qualities of the chalcocite and worsened the absorbing qualities of the chalcopyrite. Both the chalcocite and the chalcopyrite showed a Hg saturation point after five weeks of exposure to Hg vapor. The molybdenite showed no abilities for absorbing Hg in either the activated or pure form.

In conjunction with the synthesis and processing of these novel intercalation compounds, our crystalline phase identification/quantification capabilities, (i.e., procurement of PDF-2 Structure Database), and new crystalline structure modeling/analysis tools, (i.e., MSI's Cerius^2 software) put in place by another FY-98 Core Competency Project has directly enhanced our capabilities to perform solid materials characterization and analysis. The INEEL now has a set of crystalline structure analysis,

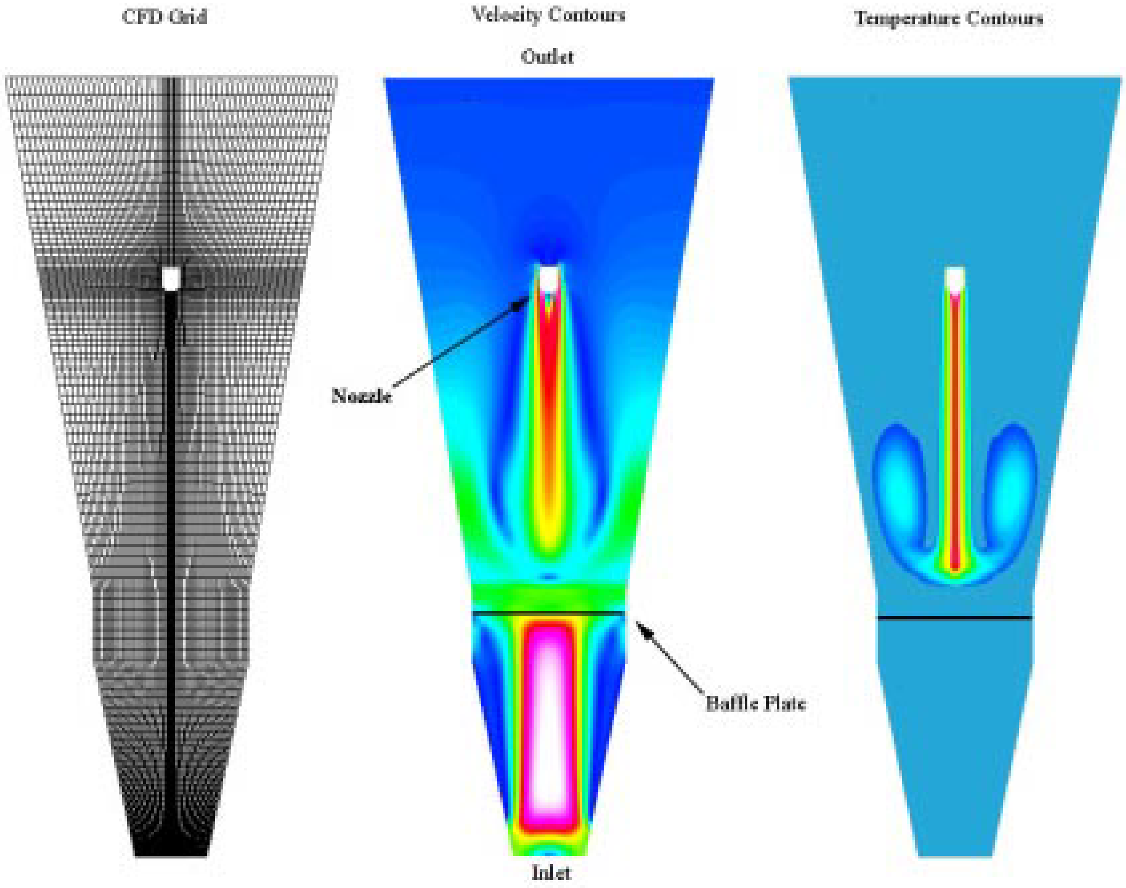


Figure 18. CFD modeling results for Glatt spray coating process.

identification, and modeling tools that will facilitate the engineering of molecular separation systems. With these new and enhanced capabilities, the process of analyzing, identifying, quantifying, and modeling crystalline materials is as follows:

1. XRD data collection using Phillips or other powder diffractometer

2. Identify crystalline phases using the PDF-2 database (a product of the International Centre for Diffraction Data)

3. Obtaining crystalline structure data of identified phase via STN international online service access to the Inorganic Crystal Structure Database (ICSD)

4. Perform multiphase Rietveld analysis of XRD data using Siroquant software, or alternatively, single phase Rietveld analysis using the General Structure Analysis System (GSAS) module in Cerius.^{2}

5. Perform electronic structure analysis on refined structures using MSI's Cerius^2 software.

Relative to our enhanced materials processing capabilities base, we have established a new controlled atmosphere calcining furnace, a rotational-casting film maker, a top-down spray coating system, and a thin film thickness measurement system. Further, we have begun to utilize the CFD modeling code "CFDLIB" for modeling the spray coating process. CFDLIB became available at the INEEL in FY-98 as a result of other Core Competencies Initiative funded effort, i.e., the projects directed by Ray Berry and Eric Greenwade.

Based on our FY-98 effort, we are in a position to focus on the development on novel molecular adsorbents/absorbents materials that include metal sulfides, transition metal oxides, and organic polymer systems.

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Advanced Strategies for Probing Structure and Reactivity at the Top Monolayer

G. S. Groenewold, J. R. Scott

Scope and Objectives

This report describes progress made during fiscal year 1998 for the title program, which is part of the INEEL Core Capabilities Enhancement project, initiated during FY-98. The objective of this program is to gain an understanding of the reaction dynamics of adsorbate (or contaminant) molecules with metal oxide surfaces, and in so doing build INEEL capability in the area of surface chemistry.

Tasks for FY 1998

The scope for this program has encompassed two tasks for FY 1998:

1. Investigating aluminosilicate oligomeric anions and their reactivity. This includes development and application of secondary ion mass spectrometry (SIMS) methods for characterizing adsorbate species on surfaces.

2. Development of staff and instrumental capability that will permit application of novel surface interrogation approaches to the chemistry of significant contaminant-surface systems.

Technical Accomplishments

Background

The development of technologies for understanding contaminant-surface chemistry has a high degree of relevance to issues currently being faced by EM. For example, most activities within the decontamination and decommissioning focus area require separating contaminant species, both organic and inorganic (including radionuclides), from industrial and environmental surfaces. Similarly, surface chemistry issues are also significant within the subsurface focus area. In the subsurface realm, interactions with surfaces determine whether a contaminant is retained, reacted, or mobilized.

Specific surfaces of interest are metal oxide surfaces having environmental or industrial significance, such as soils, minerals, steel, or cement. Much of the surface chemistry of these inhomogeneous materials has been neither identified nor exploited. A survey of the research needs for the Department of Energy (DOE) focus areas points to the need for a fundamental understanding of the environmental fate, transport, and potential manipulation of a suite of organic and inorganic chemicals which come into contact with metal oxide surfaces. The needs that were identified are either directly or indirectly related to a lack of fundamental scientific information on chemical interactions with these surfaces.[1]

Despite the importance of surface chemistry of environmental and industrial materials, it has not been the focus of extensive research. This is primarily due to two factors. The first is sensitivity. When interactions occur, the surface concentration is normally one monolayer or less, which is on the order of nanograms to picograms per mm^2. Measurement of chemicals at these levels, on naturally occurring surfaces, is difficult to do. The second factor is the inhomogeneous nature of most environmental surfaces, which acts to complicate the understanding of surface chemistry. Multiple types of surface interactions can be occurring on a microscopic level, which confuse and obfuscate interpretation of macroscopic experiments. As a consequence of these two factors, investigation of low contaminant concentrations on heterogeneous environmental surfaces have been few.

Historically, most surface chemistry investigations have been performed on more “pristine” environments associated with single crystals at high vacuum. X-ray, photon, and electron spectroscopies have been developed, and provide detailed information on the near-surface, elemental composition of the bulk sample. It is worthwhile noting that in several application areas, these surface interrogation techniques are considered to be mature. This is particularly true in catalysis, corrosion, semiconductors, and metallurgy, where single crystals can be studied under high vacuum conditions. However, these techniques do not provide information on the molecular composition of the top monolayer, which is where the controlling reaction chemistry takes place. For this reason, even though these surface analysis techniques have been applied to environmental and industrial samples, most of what is known and understood about the chemistry occurring between contaminants and environmental surfaces has originated from bulk chemical characterization.

A surface analytical technique which has shown the ability to effectively probe the top monolayer, and also to provide the spatial resolution to overcome surface heterogeneity is secondary ion mass spectrometry (SIMS). Because of the high sensitivity, high spatial resolution, and high mass resolution of SIMS, as well as the novel developments mentioned below, the technique is the focus of the metal oxide research described in the remainder of this report. SIMS as it is implemented in INEEL instrumentation provides the opportunity to characterize and study the reactivity of the metal oxide species.

The premise underlying this program is that with proper understanding of these systems, control and manipulation of the interactions would be possible, for the purpose of deliberate separation or sequestration chemistry. Knowledge of structure and chemical reactivity of inhomogeneous surfaces found in almost all environmental applications will motivate research aimed at the intentional control of surface chemistry, such that specific chemical interactions will be effected. This fundamental science will have significant long term payoffs in a variety of areas, which might include, but are not limited to modeling environmental fate and transport, decontamination of industrial surfaces, improved remediation strategies, and sensor development.

FY 1998 Accomplishments

Chemistry of $(SiO_2)_nAlO_2^-$ *Oligomers Derived from Aluminosilicate Surfaces.*

The initial approach taken in this study was to attempt to characterize the surfaces of refractory materials, specifically those containing high levels of Al and Si, using secondary ion mass spectrometry (SIMS). These systems were chosen because they represent an important category of materials that includes soils, zeolites, glasses, and other types of materials. Soil particles represent the salient substrate encountered by contaminants in the environment. For a large number of sands and clays, Al and Si represent the dominant metals in the materials. Consequently, an investigation of the SIMS chemistry of soils was undertaken.

The instruments employed for these investigations were unique SIMS spectrometers designed and fabricated at the INEEL. They differ from commercially available spectrometers (Table 1) principally in the primary projectile employed: Normally, SIMS generates secondary ions from the surface by bombarding that surface with energetic (kiloelectron volt) atomic ions. In the INEEL instrumentation, the polyatomic perrhenate (ReO_4^-) projectile is used. This projectile is formed in the gas phase by heating a unique $Ba(ReO_4)_2/Eu_2O_3$ ceramic to 800°C in vacuo.[2] The resulting gas-phase anion can then be accelerated and used to impact the sample surface. ReO_4^- projectiles significantly augment the production of molecular fragments from inorganic oxide surfaces.[3] The studies using the ReO_4^- equipped instruments were supplemented using a time-of-flight (TOF) imaging SIMS instrument equipped with Ga^+ as the bombarding projectile. This instrument is capable of high mass resolution, which permits accurate mass measurement. It also can sputter clean surfaces, which serves to eliminate hydrocarbon contamination from the silicate surfaces. The TOF-SIMS experiments were conducted in collaboration with the Image and Chemical Analysis Laboratory, which is located at Montana State University.

Initial analyses of soil particles were undertaken using quadrupole and TOF SIMS instruments (Table 1). The salient operational feature of both of these instruments is that both operate at low pressures, $< 1 \times 10^{-6}$ torr, and the ion lifetime in the secondary ion source region is short (microseconds). These features are mentioned because they differ substantially from those of the ion trap SIMS instrument employed in the ion reactivity studies described later in this report.

The cation spectra of the soil particles, collected using the low pressure quadrupole mass spectrometer, were dominated by hydrocarbon contamination, and little could be deduced that pertained to the structure of the underlying aluminosilicate. The cation spectra collected using the TOF-SIMS spectrometer were similar in that they contained abundant hydrocarbon ions. In addition, the TOF-SIMS spectra contained abundant atomic ions corresponding to Na^+, Al^+, Si^+, and K^+. The relative abundances of the atomic ions recorded using the TOF-SIMS instrument are always greater than those recorded using the quadrupole SIMS instrument. This difference reflects two factors that cannot be separated. First, ReO_4^- generates a higher proportion of molecular ions than does $Ga.^+$ Second, the TOF analyzer accommodates a wider range of secondary ion kinetic energy values than does the quadrupole; hence the TOF transmits a higher fraction of atomic secondary ions than does the quadrupole.

The anion spectra acquired using the quadrupole SIMS contained low abundance, but observable ions corresponding to silicon oxide anions, and aluminosilicate anions (Figure 1). Compositions for these ions (Table 2) were surmised based on the composition of the soil samples, as generated using energy dispersive x-ray analysis (EDX).

Similar ions could be observed in the TOF-SIMS instrument, together with substantial hydrocarbon ion signal, the latter probably derived from adsorbed organic acids. Using the TOF, the organic ion signal could be eliminated by sputter cleaning the surface using a nanoamp Ga^+ beam in the DC mode. The aluminosilicate ion signatures could then be measured again (without exposing the sample to atmosphere), and in this experiment, the exact masses and isotopic ratios could be more accurately measured. These experiments showed that the ions assigned the general composition $(SiO_2)_nAlO_2^-$ did indeed contain one Al atom, and multiple Si atoms. These species can be viewed as silicate oligomers that have been tagged with an AlO_2^-; the aluminum induces a negative charge center in the silicate matrix, which permits observation of the oligomer in the mass spectrometer. Significantly, these charge centers have also been shown to be directly responsible for cation adsorption.[4] A second interesting

Table 1. Salient features of the SIMS instruments used during the aluminosilicate oligomer studies.

Analyzer Type	Primary Projectile	Pressure Regime	Ion Lifetime
Quadrupole	5 keV ReO_4^-	10^{-7} torr	10s of microsec
Time-of-flight	15 keV Ga^+	10^{-8} torr	10s of microsec
Ion trap	4.5 keV ReO_4^-	10^{-4} torr	10s to 100s of millisec

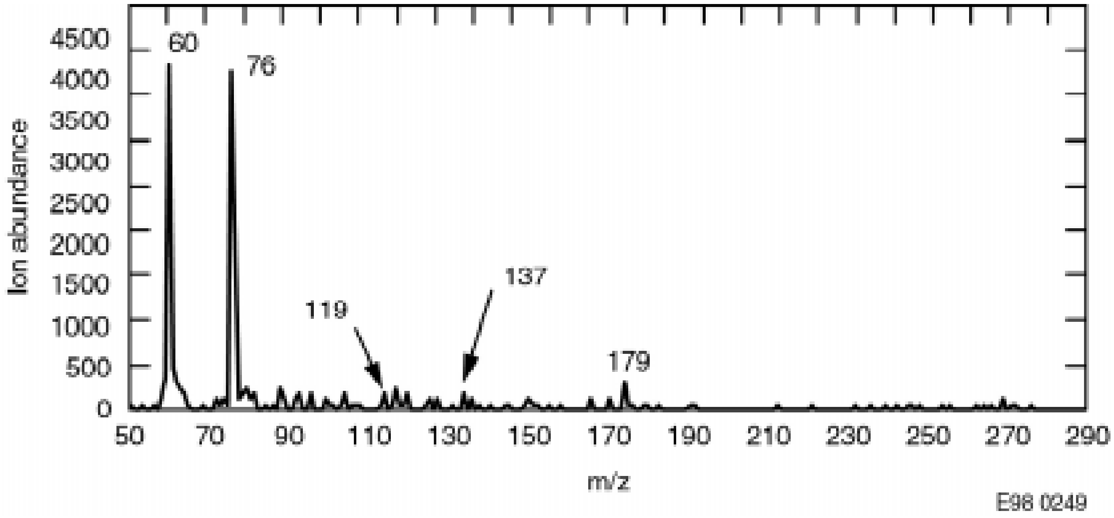

Figure 1. Anion spectrum of soil acquired using the quadrupole SIMS instrument.

Table 2. Compositions of ions observed in the low pressure anion SIMS analyses.

M/z	Composition	M/z	Composition
60	SiO_2^-	119	$(SiO_2)_1AlO_2^-$
76	SiO_3^-	179	$(SiO_2)_2AlO_2^-$
77	$HSiO_3^-$	239	$(SiO_2)_3AlO_2^-$

feature of these ions is that they are formed in a completely dehydrated state in the vacuum of a low pressure mass spectrometer. Hence they may be used for the study of ionic aluminosilicate moieties in the absence of water.

These results indicated clearly that the surfaces of refractory oxides could be interrogated directly using a SIMS approach, and that ions characteristic of the surface composition could be generated. Further, larger oligomeric species could be sputtered into the gas phase; this was especially apparent in the data acquired using the IT-SIMS (see below). This suggested that the reactivity of the trapped, aluminosilicate oligomers could be studied by admitting volatile contaminant adsorbate molecules. The single drawback to the work was the fact that the abundances of the aluminosilicate oligomers, as generated from soil surfaces, was low.

To improve the secondary ion abundance of the aluminosilicate oligomers, a series of zeolite materials were analyzed. The zeolites examined had a range of pore sizes (3 to 10 Å) and a variety of counter cations (Na^+, K^+, and Ca^{++}). It was felt that the higher Al content of the zeolites would facilitate the formation of the aluminosilicate oligomeric anions, and this proved to be correct. Compared with the soil samples that had been studied, the abundance of the $(SiO_2)_nAlO_2^-$ species was enhanced anywhere from 2 to 10 times (Figure 2).

Further analysis was performed on the zeolite samples in which the original cations (Na^+, K^+, Ca^{++}) had been exchanged with Cs^+. SIMS analysis of the Cs^+-exchanged zeolites showed enhanced emission of the SiO_n^- and $(SiO_2)_nAlO_2^-$ species compared to the unexchanged samples. Specifically, emission of SiO_n^-, n = 1,2, was enhanced by a factor of 2 to 3 times (Figure 3). Emission of $(SiO_2)_nAlO_2^-$, n = 1,2,

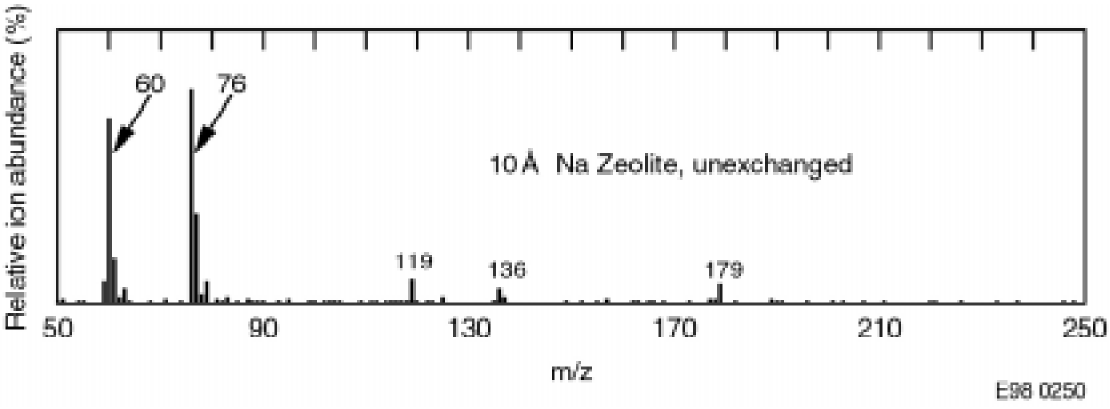

Figure 2. Quadrupole-SIMS anion spectrum of Na zeolite sample.

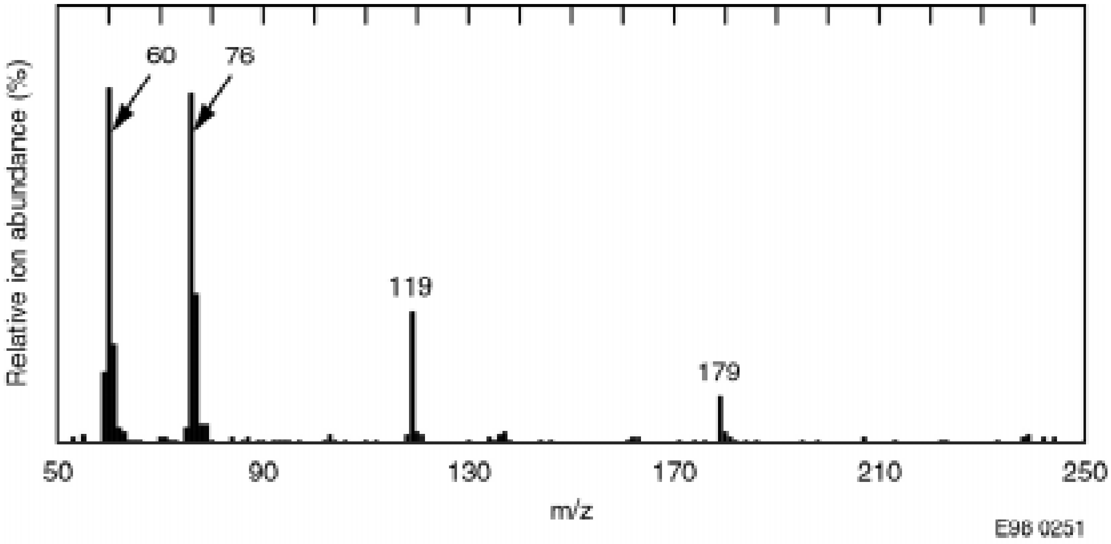

Figure 3. Quadrupole SIMS anion spectrum of Cs^+-exchanged zeolite sample. Y axis (ion abundance) is comparable to that in Figure 2.

was enhanced 5 to 7 times. It was concluded that Cs^+ exchange not only enhanced the absolute amount of the aluminosilicate-derived ions, but also enhanced the relative fraction of the oligomeric anions sputtered from the surface.

The surprising enhancement of the secondary aluminosilicate anions is interpreted in terms of Cs^+-substitution lowering the work function of the aluminosilicate surface, the consequence of which is a more facile formation of ionic sites on the surface. This in turn leads to the formation of more abundant aluminosilicate anions in the gas phase upon ion bombardment. The observation may have implications that extend beyond the present study. If metal leaching is inhibited by ionic sites on the surface of silicate glass waste forms, then this finding suggests that more effective glass forms may be engineered by replacing the cations on the surface with Cs^+. Since Cs^+ is perhaps the most strongly binding cation, this may well be a means to form a relatively permanent ionic barrier at the surface of glass waste forms.

The zeolites were subsequently analyzed using an ion trap (IT) SIMS instrument,[5] which is unique to the INEEL. This type of instrument is equipped with the ReO_4^- primary ion. As indicated above, the operational attributes of the IT-SIMS are substantially different from those of the quadrupole or the TOF instruments. The IT-SIMS operates at an analyzer pressure of approximately 1×10^{-4} torr He, and ion lifetimes in the analyzer are typically 10s to 100s of milliseconds, and can exceed one second. These factors, together with the fact that the modest vacuum in the IT-SIMS results in substantial H_2O and other gases in the spectrometer, combine to make the IT-SIMS experiments substantially different from those performed in the low pressure instruments. The ion trap has no inherent high mass discrimination, as does the quadrupole. Further, the presence of the thermal He bath gas in the device serves to thermally stabilize secondary ions which are internally 'hot.' The result is that many ions which are not observable using the quadrupole or ToF are frequently observed in great abundance using the ion trap. This is because the ion trap is more effective at analyzing higher mass, or chemically more fragile ions.

The IT-SIMS functions effectively as an ion-molecule reactor for secondary ions in the gas phase. In the present set of experiments, the neutral molecule that was used to react with the aluminosilicate oligomers was H_2O—initially the residual H_2O in the system was used as a reactant, and later D_2O was deliberately admitted to the IT-SIMS in order to study the reactivity (Figure 4). The latter experiment shows that any volatile reactant may be studied in this manner, and demonstrates that a virtually unlimited set of reactivity experiments is possible using neutral, volatile reactants. Since in the IT-SIMS ionization and mass analysis are separated by a variable amount of time, the extent of the reaction can be easily followed.

The IT-SIMS has another important capability that distinguishes it from the other two SIMS instruments. It is capable of ion isolation and fragmentation, *i.e.*, MS^n. This capability permits the

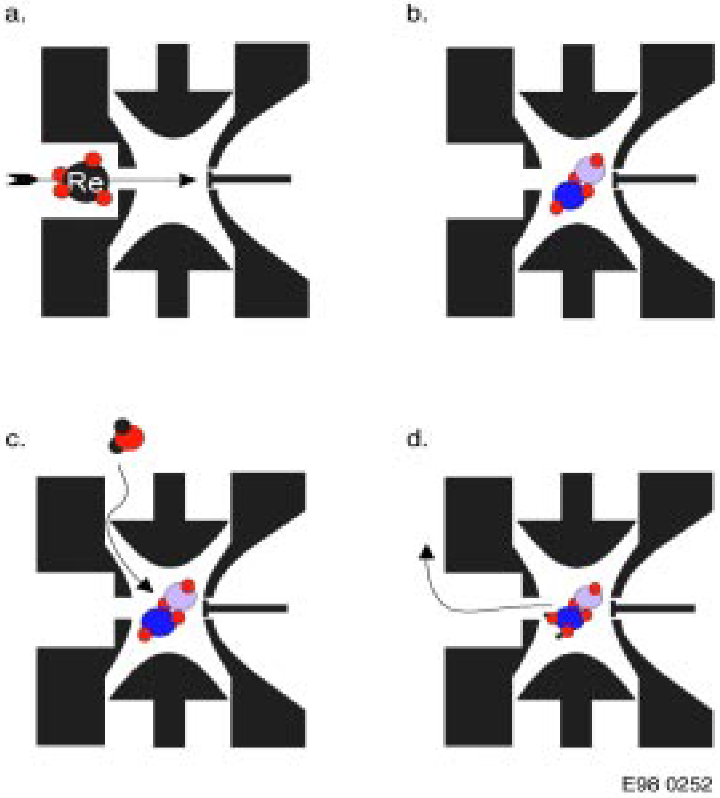

Figure 4. Schematic diagram of ion molecule reactivity studies performed in the IT-SIMS. a. ReO_4^- projectile fired across IT, where it impacts sample (zeolite, soil particles); b. aluminosilicate ion ($(SiO_2)_1AlO_2^-$ shown) desorbed into the gas phase, and isolated in the IT; c. Gaseous reactant admitted to the IT (D_2O shown); d. reaction of $(SiO_2)_1AlO_2^-$ with D_2O to form $(DO)_2SiOAlO_2^-$; product ion is scanned out of the trap where it is detected.

isolation of the ion of interest, whereupon it may be either further energized, so as to cause fragmentation, or allowed to react at its ambient temperature with neutral molecules in the trap. These processes are in fact probes of the reactivity of the ion (both unimolecular and bimolecular, respectively), which can be used to characterize ions and also to probe fundamentals of reaction dynamics of the species.

When the Cs^+-exchanged zeolites were analyzed using the IT-SIMS instrument, the spectra were qualitatively similar to those recorded using the low pressure instruments: ions were observed corresponding to SiO_n^- and $(SiO_2)_nAlO_2^-$. However, oligomeric ions having higher masses were more easily observed using the IT-SIMS (Figure 5): ions up to n = 5 were well above background. Furthermore, the addition of H_2O to the oligomers was observed at masses corresponding to $(SiO_2)_nAlO_2^- \bullet mH_2O$, where m = 1, 2 or 3. The abundance of the hydrated ions could be augmented by increasing the reaction time, *i.e.*, the time between ionization (sample bombardment) and detection (scan out). When the reaction time was increased, the abundance of $(SiO_2)_nAlO_2^-$ decreased, while $(SiO_2)_nAlO_2^- \bullet H_2O$, and $(SiO_2)_nAlO_2^- \bullet 2H_2O$ dramatically increased (Figures 6, 7). Interestingly, up to n = 3, no more than two H_2O were observed to add to $(SiO_2)_nAlO_2^-$. However, for n > 3, a third H_2O could be observed adding to the ions.

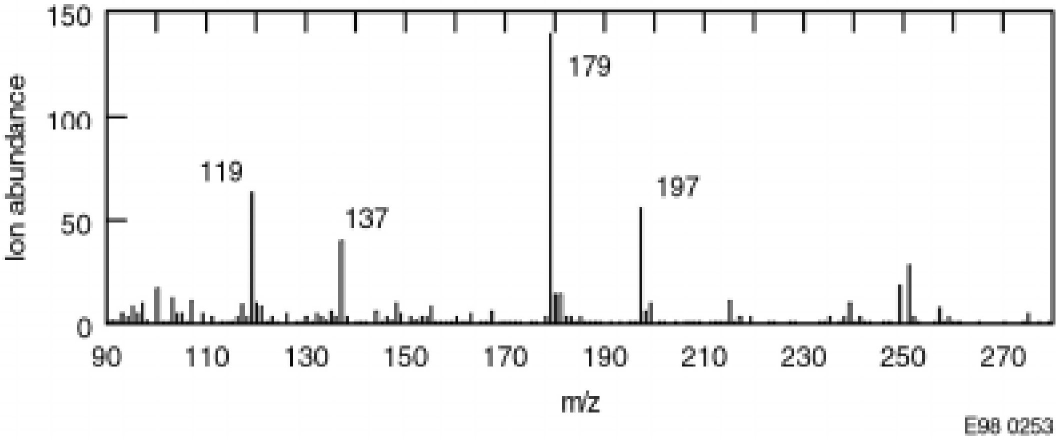

Figure 5. Anion IT-SIMS spectrum of Cs^+-exchanged zeolite, total reaction time 0 milliseconds.

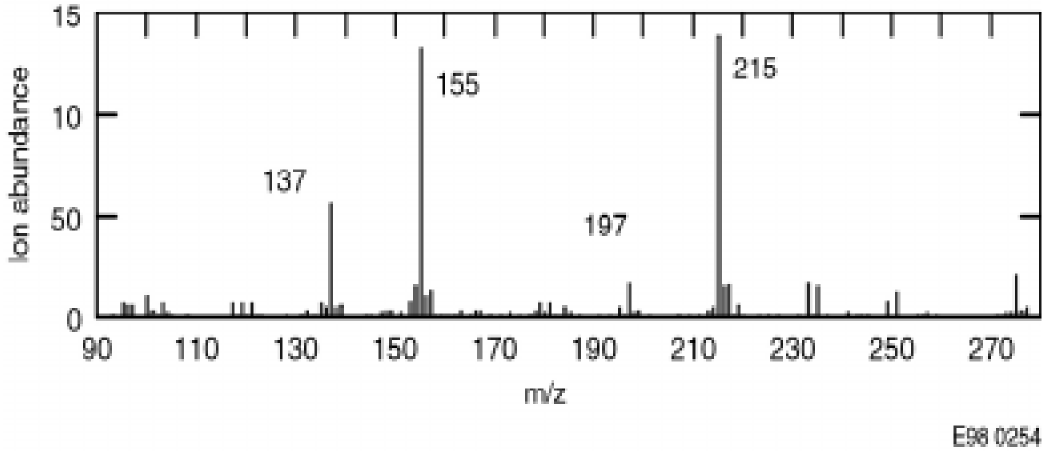

Figure 6. Anion IT-SIMS spectrum of Cs^+-exchanged zeolite, total reaction time 300 milliseconds.

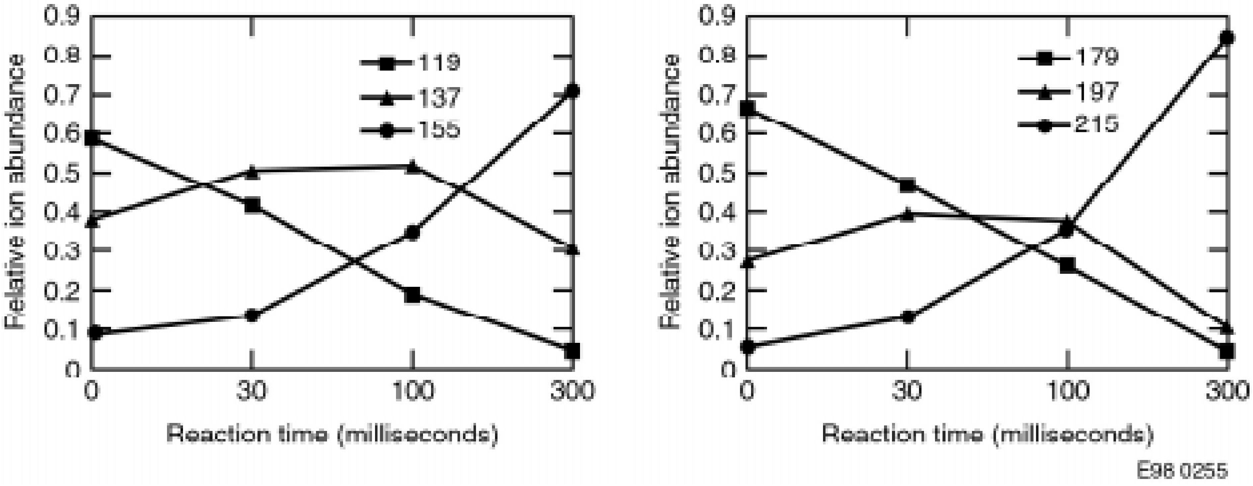

Figure 7. Fractional ion abundance as a function of reaction time in the IT-SIMS. a. Reaction of $(SiO_2)_1AlO_2^-$. b. Reaction of $(SiO_2)_2AlO_2^-$.

D_2O was deliberately admitted to the IT-SIMS in order to verify the reaction with water, and also to confirm the assignments of the ion compositions. Ions in the IT were allowed to react for approximately one second, at a pressure of 2×10^{-6} torr D_2O. The mass spectra recorded after this time revealed substantial D for H exchange in the hydrated ions, and hence indicated the number of H atoms in the composition of the ion. For example, *m/z* 155 was shifted to *m/z* 159 (as well as 156-158), but not to 160 (Figure 8). The maximum D-for-H mass shift of 4 amu is consistent with the proposed composition $(SiO_2)_1AlO_2^-{\bullet}2H_2O$, which has four exchangeable H atoms. However, the shift is not consistent with the composition $(HO_2Al)AlO_2^-{\bullet}2H_2O$, which would have five exchangeable H atoms. Using the same approach, the composition of $(SiO_2)_2AlO_2^-$ was validated. Further D_2O substitution experiments have not been performed to date, but the potential of this approach for identification of the number of exchangeable H atoms is indicated clearly.

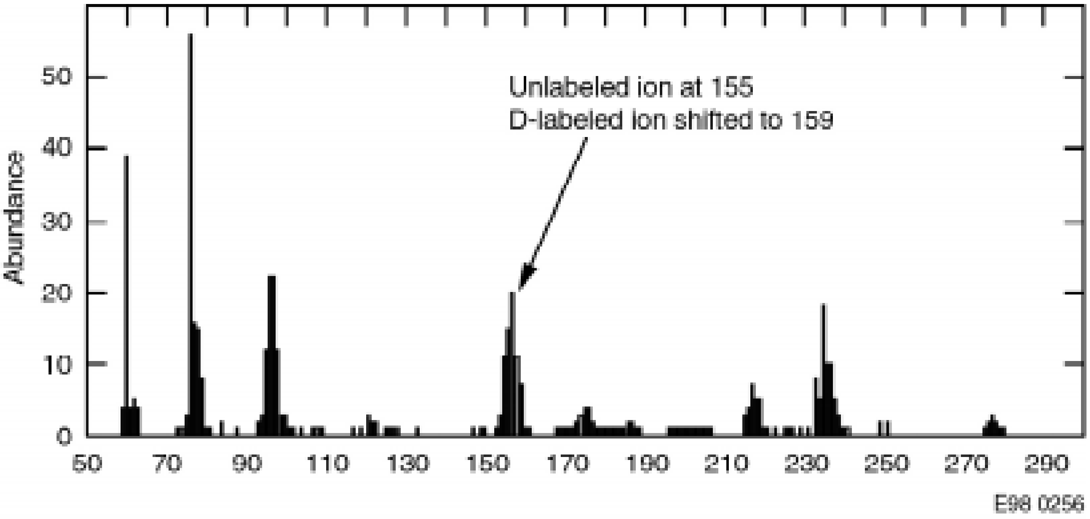

Figure 8. Anion IT-SIMS spectrum of Cs^+-exchanged zeolite, reaction time 300 msec, in the presence of 2×10^{-6} torr D_2O.

In order to understand the reactivity of the aluminosilicate oligomers, studies were performed to assess the H_2O reaction of the monomeric aluminate and silicate ions AlO_2^-, SiO_2^-, etc. Substantial differences in reactivity were observed. The most reactive ion was observed to be AlO_2^-, which readily added one and two H_2O molecules to form *m/z* 77 and 95, respectively (Figure 9). This experiment was performed by bombarding alumina and isolating *m/z* 59 (AlO_2^-). Unsurprisingly, the formation of the dihydrate occurs in a stepwise fashion: Isolation of the monohydrate ($(HO)_2AlO^-$) followed by a reaction time resulted in rapid formation of the dihydrate.

The reactivity of the radical anion species $HOAlO_2^-$ was also probed. This species will react by abstracting a H atom (presumably from H_2O) to form *m/z* 77, which then reacts with H_2O to form *m/z* 95 as above. In addition, the $HOAlO_2^-$ radical will also react directly with H_2O to form a product ion at *m/z* 94. It is possible that this species will also react with water by H atom abstraction.

In contrast to the aluminum species, the radical SiO_2^- is unreactive with H_2O. This ion was made by bombarding a zeolite sample, and isolating *m/z* 60. After reaction periods as long one second, no product ions could be observed. In a second experiment with this target, *m/z* 76 was isolated, which is SiO_3^-. This ion was very nearly completely unreactive with H_2O. After one second reaction time, a very small H_2O adduct ion was observed at *m/z* 94, but the abundance of *m/z* 76 was nearly unchanged. The small amount of reaction observed may be due to the presence of the isobaric aluminum species.

The ion at *m/z* 77 originating from the zeolite was also isolated and allowed to react. This ion readily added H_2O to form *m/z* 95. The rate of water addition was nearly identical to that observed for the *m/z* 77 isolated in the alumina experiments, which suggests that this ion may have the composition $(HO)_2AlO.^-$ However, $HOSiO_2^-$ cannot be ruled out. This ambiguity points to the need for pure silica experiments, which have not yet been performed.

The reactivity studies performed using aluminum and silicon oxide anions permit some speculation regarding the reactivity of the oligomeric $(SiO_2)_nAlO_2^-$ species. Since both the aluminosilicate oligomers and AlO_2^- react readily with two H_2O molecules, one might surmise that the aluminum oxide moiety is responsible for the reactivity observed in the aluminosilicate oligomers. On the other hand, an AlO_2 moiety may induce a reactive center at an adjacent silicon oxide moiety. Since the structure of the aluminosilicate oligomers cannot be probed directly using vibrational spectroscopic methods, studies employing computational techniques have been initiated in collaboration with Dr. J. B. Wright, Aberdeen Proving Ground.

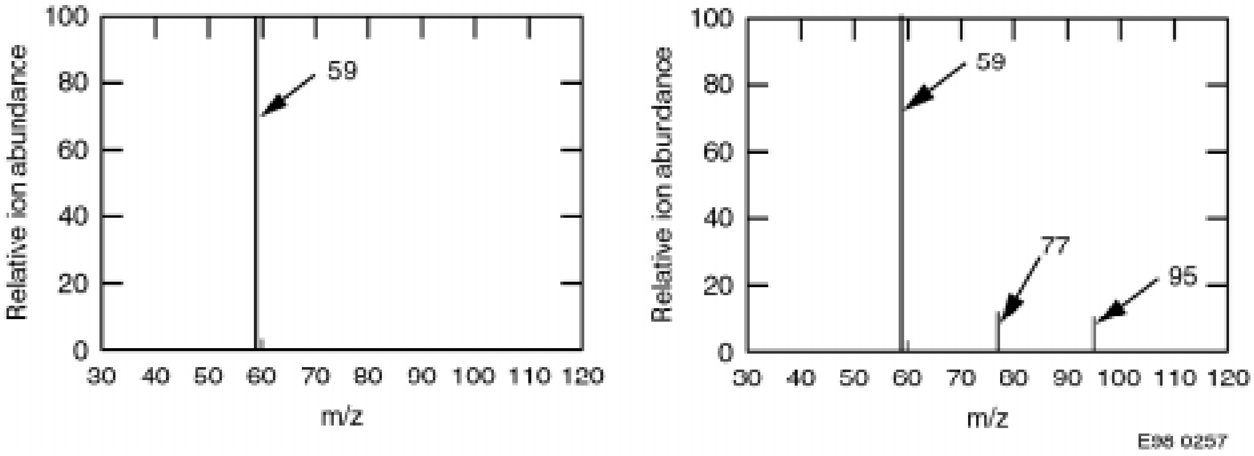

Figure 9. Anion IT-SIMS spectrum of alumina, where AlO_2^- was isolated, and allowed to react with H_2O: a) reaction for 36 milliseconds, b) reaction 172 milliseconds.

Ab initio calculations were performed using the Gaussian 94 package, at the B3LYP/6-31G(d) level. The most extensively studied system has been $(SiO_2)_2AlO_2^-$. Structural minimization revealed two 6-membered ring structures a̲ and b̲, which were competitive in terms of ΔH_f, within two kcal/mol (Figure 10). Structure c̲ minimized at 44 kcal/mol; if interconversion pathways exist, this possibility will clearly not be favored. Significantly, no minimization was achieved for any acyclic structure. The lowest energy structure a̲ contains a trigonally coordinated AlO_3 moiety in which each oxygen is in turn bound to a Si. Structure a̲ also contains a trigonally coordinated SiO_3 moiety, in which one of the oxygen atoms is singly coordinated; we interpret this site in terms of a silylyl moiety Si=O. The second silicon atom is tetrahedrally coordinated to four O atoms, where one of the O atoms is singly bound. This is where the negative charge is likely localized.

A similar analysis of structure b̲ reveals that both Si atoms and the Al atom are each trigonally coordinated to three O atoms, one of which is singly coordinated. In the case of the Si atoms, this is interpreted in terms of a silylyl moiety Si=O, which satisfies the valence requirements of Si. In the case of the Al atom, the singly coordinated O atom must carry the negative charge. Hence, the two proposed structures may have substantially different chemistry.

The reaction chemistry of structure b̲ with water was also probed using the ab initio approach. In this initial study, the H_2O molecule was brought into proximity with one of the silylyl moieties. The reaction proceeded to add H_2O to $(SiO_2)_2AlO_2^-$, forming an adduct that minimized on a gem-diol structure. This result may be mechanistically at odds with the results for water reactivity with SiO_2^- and

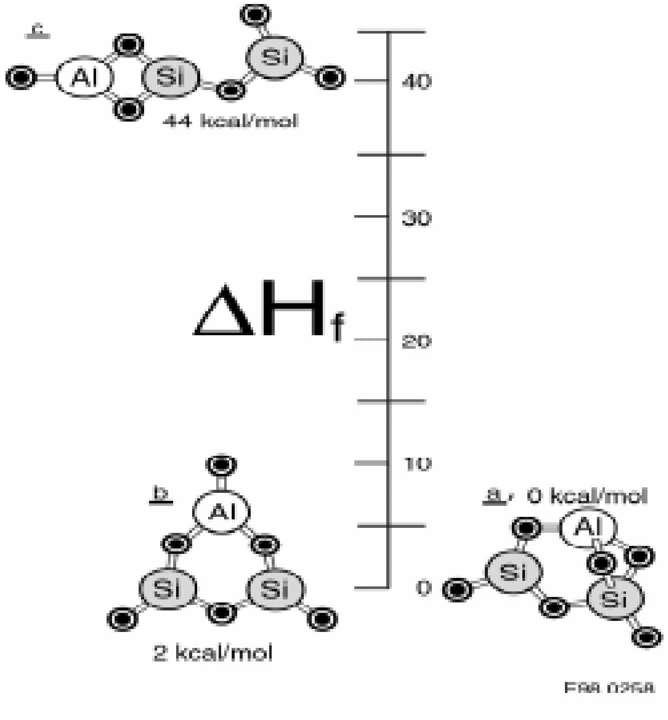

Figure 10. Structures for $(SiO_2)_2AlO_2^-$ generated using *ab initio* calculations. The energy scale represents relative enthalpy of formation, in kcal/mol.

AlO_2^-, which suggests that reaction should occur at the aluminate anion site, but not at a silylyl. However, it is significant that the reaction was approximately 65 kcal/mol exothermic, and that no reaction barrier could be identified. This suggests that $(SiO_2)_2AlO_2^-$ is highly reactive, which is consistent with the ion trap reactivity studies. Clearly, the ab initio studies must be extended to include scenarios where H_2O is brought initially into proximity with the AlO^- moiety.

Instrument Development

The initial studies performed on aluminosilicate matrices showed that a broad range of heretofore unexplored chemical reactions could be addressed by using ion bombardment of surfaces in conjunction with trapped ion mass spectrometry such as the IT-SIMS instrument. However, using the IT conferred several inherent limitations on this line of research, and these have precluded the acquisition of information necessary to rigorously characterize the metal oxide reaction chemistries. The IT constitutes a relatively “dirty” environment in which to perform gas-phase ion chemistry. The background pressure is typically on the order of 1×10^{-6} torr, and this atmosphere contains substantial H_2O. This is an advantage when studying qualitative aspects of water addition chemistry, but is a problem when investigating other reactants (e.g., D_2O). A second problem is that at its the present state of the art, the IT has limited mass resolution, which is a hindrance for the identification and isolation of isobaric ions (same nominal mass different elemental composition). An example of isobaric ions which cannot be distinguished using the ion trap is $(SiO_2)_1(AlO_2H)AlO_2^-$ (accurate mass of 178.91727), and $(SiO_2)_2AlO_2^-$, (178.90485). A mass resolution ($m/\Delta m$) of 14,000 is required in order to separate these compositions, which is far beyond the capabilities of IT instrumentation at this time.

The IT also has limitations associated with mass range. Commercially available IT instruments, on which the IT-SIMS instruments are based, have an upper mass range of 640. In the case of the $(SiO_2)_nAlO_2^-$ systems, this limit dictates that the largest measurable ion would correspond to $n = 9$ (without any adduct formation). Since the larger oligomeric species are expected to more closely imitate condensed phase surfaces, the mass range limitation constitutes a hindrance, which will become more acute when large, biomolecules are studied on metal oxide surfaces. The generation of higher mass species may also become problematic, even when using the polyatomic projectile. Thus an instrument possessing advanced surface disruption techniques would be desirable. A final limitation associated with the current IT-SIMS instrumentation is that only systems in which the metal oxide is ionized can be investigated. Chemical systems in which the adsorbing species is ionized, and the metal oxide is neutral, cannot be probed.

The desire to perform investigations beyond the instrumental envelope defined by the IT-SIMS has motivated the design and fabrication of an alternative instrument having capabilities in those areas that cannot presently be addressed. This instrument is based on a Fourier Transform Mass Spectrometer (FTMS), and will have both particle and photon surface desorption capabilities. The FTMS, like the IT, is a trapped ion device capable of ion isolation, and subsequent condensation or fragmentation reactions. However, the FTMS is capable of handling ions having a much higher mass, at much higher mass resolution (unit mass resolution is routinely available for ions having *m/z* of 15,000). In addition, the FTMS is capable of high mass measurement accuracy, which is needed for identification of elemental compositions.

The FTMS operates at ultrahigh vacuum conditions (10^{-9} torr), which means that the reaction atmosphere within the instrument can be carefully controlled. This will permit the execution of experiments under single reaction conditions, which will in turn allow the measurement of reaction kinetics without competing side reactions.

The FTMS instrument will be equipped with both particle desorption (ReO_4^- bombardment), and with photon desorption (Nd:YAG laser). The utilization of the laser will permit several new experiments that cannot be performed at present. Laser desorption, especially when combined with an organic matrix, may allow the generation of gas-phase metal oxide species having masses in excess of 1,000 amu. Second, the combination of laser irradiation with particle bombardment of the same surface represents a second strategy for getting higher mass species into the gas phase: adding ReO_4^- bombardment to a surface that has already been excited by photon irradiation may result in improved efficiency for higher mass secondary ion production. A third intriguing possibility is the utilization of the laser to generate ionic metal (or organic) reactants, which can then be reacted with neutral metal oxide molecules generated by the particle desorption event. This would open yet another new realm of metal oxide reaction chemistry currently not accessible for study at the molecular level.

A Fourier transform mass spectrometer is composed of four main parts (Figure 11): a superconducting magnet, vacuum system, data acquisition and control system, and ionization source(s). There were four main goals in the design of the FTMS at INEEL: 1) a high enough magnetic field to ensure high mass resolution and mass accuracy; 2) a vacuum system that can operate over a range of pressures from 10^{-4} down to 10^{-9} torr to facilitate reaction-pathway studies; 3) an oil-free vacuum system to maintain pristine samples; and 4) incorporation of a variety of ionization methods, including a custom perrhenate (ReO_4)source.

Although not very common, both internal[6] and external SIMS using atomic ion beams have been demonstrated with FTMS instruments.[7,8] However, an internal, polyatomic ion beam has not been incorporated into an FTMS. As mentioned above, polyatomic ions offer the advantage of sputtering large, molecular ions from surfaces. The advantage of internal versus external ion generation is two-fold: 1) higher abundance of ions sputtered from the surface can enter the cell and 2) less discrimination between ion populations of different masses, because the ions do not have to be guided through external ion-optic lenses into the cell, as is the case when they are externally generated.

A 7 Tesla superconducting magnet (Oxford Instruments, UK) has been installed at the INEEL. The data acquisition and control system (Finnigan FT/MS, Madison, WI) running Odyssey program software version 4.1.1 (Finnigan FT/MS, Madison, WI) has been procured and set up. A vacuum system using three CT-8 cryopumps (CTI-Cryogenics, Waltham, MA) is presently being installed.

Four ionization sources are currently planned for the FTMS: electron impact, laser desorption, cesium ion (Cs^+) desorption, and perrhenate ion (ReO_4^-) desorption. Components for electron impact, laser desorption and the Cs^+ gun (Antek, Palo Alto, CA), have been procured. For versatility, a Nd:YAG laser (Continuum, Santa Clara, CA) was selected with a pulse width of 4−7 nanoseconds at the four wavelengths: 1,064 nm, 532 nm, 355 nm, and 266 nm. Initial design of the custom ReO_4^- source has been done using SIMION 7.0 (internationally recognized simulation program for mass spectrometer development, designed at the INEEL by Dave A. Dahl).

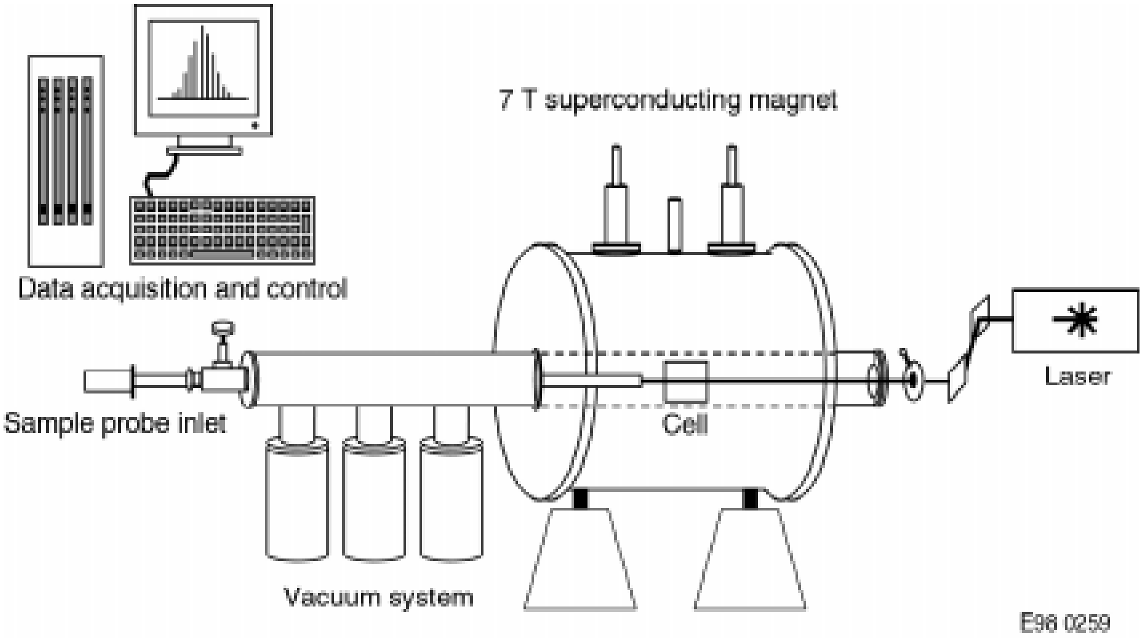

Figure 11. Conceptual diagram of combined laser desorption-, particle desorption-FTMS.

Summary

The most critical venue for EM is found at the solid surface interface. In this realm occurs those processes that are controlling relative to contaminant sequestration, destruction, or mobilization. The clear understanding of contaminant surface reaction dynamics, specifically on metal oxide surfaces, has long been recognized as a prerequisite by those wishing to control and manipulate these processes. The research conducted in the present project has resulted in the development of techniques that permit the investigation of metal oxide-contaminant interactions at the molecular level. Initial studies have shown that aluminate, silicate and aluminosilicate oligomeric anions can be abundantly produced in their dehydrated states, using an IT-SIMS instrument. This phenomenon has been exploited to monitor hydration chemistry as a function of time using the IT-SIMS. These results have shown that the AlO_2^- moiety is highly reactive toward H_2O, but that SiO_2^- is not. This may imply that intentional engineering of AlO_2 moieties into glass matrices could result in surfaces having augmented contaminant adsorption characteristics. Given that a relatively short period of investigation has yielded a rich field of chemical information, it is reasonable to expect significant advances in contaminant-metal oxide surface chemistry, as the research is extended to contaminants beyond water, and to metals beyond Al and Si.

To realize the potential of this field of research, a state-of-the-art FTMS instrument is currently under fabrication. This instrument, equipped with both particle desorption (SIMS) and photon desorption (LDMS), will provide high mass, high mass resolution, and enhanced surface interrogation capability. The instrument will also afford researchers with a high level of control over the gas-phase reaction atmosphere, which will permit a significantly more rigorous characterization of the reaction dynamics. This instrument, in conjunction with the emerging IT-SIMS instrumentation, will comprise a powerful and unique instrumental capability for interrogating, and eventually understanding contaminant-metal oxide surface systems.

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BIOCHEMICAL AND GEOCHEMICAL REACTIONS ON ENVIRONMENTAL SURFACES

**W. F. Bauer, P. Pryfogle, J. Barnes, T. Ward, M. Hamilton,
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Scope And Objectives

The overall objective of this program is to develop a set of analytical of methods for determining chemical speciation and reaction mechanisms affecting the interaction of selected contaminants and biologicals with relevant surfaces under “ambient” conditions. The development of techniques and methodologies only serves a useful purpose if they can be applied to the investigation of real problems. These methods are expected to help resolve a number of questions about environmental surface chemistry that have not been accessible to date. The methods developed will be applied to a range of specific problems with relevance to DOE-EM and issues in environmental science. The work will be a strong collaboration between chemists, microbiologists, and geochemists.

To meet this objective, the following milestones were established for FY-98.

- Identify and hire a Ph.D. candidate to complement existing INEEL capabilities
- Evaluate commercial near-field scanning optical microscopic (NSOM) capabilities for program applicability
- Prepare a detailed science plan.

There were three tasks for 1998.

1. Analytical Developments
2. Biological/Geochemical Methods/Systems
3. Factors influencing chemical transport.

Technical Accomplishments

Background

At almost all DOE sites, contamination by toxic and radioactive chemicals is a problem. The contamination issues are mainly associated with a history of facility usage and disposal of organic chemicals, radionuclides, and metals directly to unsecured subsurface repositories or containment facilities that have leaked. Many of these chemicals are known or potential environmental hazards that represent a threat to water supplies and ecosystems. The presence of these contaminants can also hinder cleanup efforts such as in the decommissioning and decontamination (D&D) of facilities. In almost every case, surface chemistry plays a significant role in the fate and transport of a given contaminant. Chemical reactions and microbial processes at mineral-water interfaces will significantly influence the types of kinetics and chemical transformations of the contaminants. In addition, sorption processes will influence transport and bioavailability of contaminants. As a result, surface chemistry can influence the ease of cleanup in D&D operations, the transport of the contaminants through the environment, the stability of contaminants in “remediated” areas, and any natural attenuation processes that occur. This important role of surface chemistry to many of the existing problems within DOE is supported by two recent assessments of DOE EM technology and research needs.[1,2] These assessments identified many needs that are either directly or indirectly related to the surface chemistry and surface interactions of a variety of contaminant species and biological components with many different materials.

All of the following milestones were achieved:

- Identify and hire a Ph.D. candidate to compliment existing INEEL capabilities
- Evaluate commercial near-field scanning optical microscopic (NSOM) capabilities for program applicability
- Prepare a detailed science plan.

Specific project scope and the details behind them are identified in the science plan and are summarized by task below.

Task 1. Analytical Developments

The objective of this task is to develop analytical instrumentation, methods and techniques to address specific problems in the tasks outlined below. An important question regarding reaction kinetics at surfaces and in the presence of microbial activity is how chemical processes are spatially resolved on a microscopic scale. Therefore, particular attention is being placed on optical microspectroscopic techniques since they hold the most promise for the direct observation of chemical activity inside and outside of cells, on or near cell or mineral surfaces, and in the interfacial regions such as those where a surface is separated from the bulk solution by a thin film. Spectroscopic techniques are initially being focused on fluorescence techniques since many of the readily available probes for chemical activity are fluorescent. Fluorescent indicators are sensitive either to accumulation of the dye, a shift in the fluorescence spectrum, a change in the fluorescence lifetime or fluorescence quenching. Raman microspectroscopy will also be investigated to evaluate its potential application to determining chemical speciation on a microscopic level. Specific instrumental improvements or enhancements are to be undertaken as appropriate.

In order to expand the capabilities of the laser scanning confocal microscope (LSCM) and near-field scanning optical microscope (NSOM) for direct chemical speciation work and to minimize interferences, these instruments will be modified so that they can perform fluorescence lifetime measurements. Spectroscopic capabilities will also be added to the NSOM. The capability enhancements to the NSOM will include refining the collection optics to enhance the light collection efficiency, directing the collected light to a monochrometer/spectrograph, and measuring the signal with sensitive photon counting detectors.

The various modes of standard atomic force microscopy (AFM) will be explored to visualize the effects of surface chemistry, identify structures involved in surface interactions, to study mechanisms of microbial attachment to mineral surfaces, and to track biofilm development. Work will ultimately include observations of microbe/surface interactions in aqueous environments. Observation cells and techniques will need to be developed in order to observe the interactions under both aerobic and anaerobic environments. When possible and appropriate, SEM and XPS will be used to support the data interpretation and validate the work.

Task 2. Biological/Geochemical Methods/Systems

Subtask 2.1: Fe-reducing Bacteria. A thorough understanding of the iron cycle in an environmental system is necessary to formulate a complete picture of the biogeochemistry in that system. This subtask will focus upon iron-reducing bacteria and their role in the iron cycle of basalt formations. It is apparent that knowledge of the pH and redox potential inside the cell, in the cell membrane and outside of the cell is important to determine the appropriate redox chemistry associated with microbial iron reduction. Fluorescence microspectroscopy, NSOM and confocal microscopy will be used with appropriate fluorescent indicators to determine pH, redox potential and metal ion concentrations[3,4] of Shewanella alga cultures in contact with iron-bearing minerals. This work will enable us to examine the microchemical environments interior and exterior to the cell membrane, at the interfacial zones of the bacterium with a mineral surface, and within the biofilms that may develop on the surface. The location of the metal reduction and presence of metal ions in relation to the cells may also be directly observable with this type of methodology. Specific experiments and techniques are being designed to directly examine the chemistry of systems with living S. alga cells. Initial work will conducted with a single bacterial strain, Shewanella alga, and simple Fe^{3+} bearing oxide surfaces. Later work will involve the use of other microbial species, e.g., bacteria collected from the subsurface at the INEEL and more complex iron-bearing mineral phases, including polished basalt surfaces.

It is also important to understand the nature of the microbial contact or attachment to iron-bearing mineral surfaces and how this attachment changes under various conditions. Scanning probe microscopic (SPM) techniques are being utilized to study the interaction of the microbes with polished mineral and basal surfaces and the development of biofilms. Tapping mode atomic force microscopy (TMAFM) is the primary SPM technique being used. Ultimately, Raman microspectroscopy may also be employed to study and map the changes in the surface mineral and organic distribution on a mineral exposed to iron-reducing bacteria.

Because of the nebulous chemical knowledge concerning the “iron-reducing enzyme(s)” used by iron-reducing bacteria to transfer electrons to iron, we are also trying to isolate the proteins responsible for iron reduction in selected bacteria. Since the most likely class of proteins responsible for this reduction chemistry is cytochromes located in the cell membrane, focus has been upon identifying cytochrome-like compounds using chromatographic, spectroscopic, and electrochemical techniques. The spectroscopic and electrochemical data on the “iron-reducing enzymes” identified will ultimately be compared to the observations from the work using the pH and redox potential fluorescence probes described above. The direct interaction of the compounds identified with iron-reducing potential will then be tested with various iron-bearing mineral surfaces, iron species in solution, and other potential contaminant species such as Co and UO_2^{2+}.

An additional goal within the scope of this subtask is to create iron-bearing mineral surfaces with characteristics that are conducive to surface study while still maintaining the desired chemical characteristics of the mineral. The surfaces should be flat with very little roughness. Polishing the surfaces of some minerals is inherently difficult and obtaining pure crystals of many minerals is rare. Therefore, obtaining mineral surfaces with the desired characteristic via sputtering is being pursued.

Subtask 2.2: Interaction of TCE-Degrading Bacteria with Mineral Surfaces. A considerable amount of research has been conducted concerning solution phase degradation of chlorinated solvents by aerobic bacteria. This subtask will extend that knowledge by investigating how those interactions may be altered in the presence of mineral surfaces. The specific objective is to determine how mineral surfaces interact with or change the degradative capabilities of microorganisms capable of co-metabolic degradation of chlorinated compounds.

In order to explore that question fully, it is first necessary to understand the relationship between the bacterium and the mineral surfaces. Initially, detailed studies are to be designed and conducted to evaluate microbial attachment and biofilm formation on representative basalt minerals. A small number of pure phase minerals relevant to basalt will be investigated and, ultimately, the more complex, heterogeneous basalt will be evaluated. A common, known degrader of trichloroethene (TCE), *Burkholdaria (Pseudomonas) cepacia*, and a bacterium common to Test Area North (TAN) subsurface samples, *Pseudomonas putida*, were selected for initial experiments. Experiments will be designed to answer the questions:

> How many bacteria remain in the planktonic phase and how many attach per gram mineral or per unit surface area? Is there a preference for attachment to specific mineral phases?
>
> Is a biofilm formed, or is there simply random attachment, and how does this formation vary with mineral phase?
>
> What is the biofilm/bacterial structure at the time of equilibrium (when attachment and detachment occur at the same rate)?
>
> What is the mechanism of attachment (ionic, hydrophobic, extra-cellular polymer)?

Based on the results from the interactions of individual, selected bacteria with specific mineral phases, experiments will be designed that incorporate contaminant addition at varying concentrations. These experiments will be designed to evaluate the differences in degradation rates observed for different degrees of bacterial attachment. Specifically, the hypothesis that the mechanism of attachment influences the rate of co-metabolism of chlorinated solvents will be investigated. TCE degradation by aerobic methanotrophs and toluene/phenol degraders will be evaluated first. However, experiments are planned to investigate reductive dechlorination of PCE and carbon tetrachloride by anaerobic bacteria as well, once the analytical techniques have been fully developed.

Task 3. Factors Influencing Chemical Transport

Subtask 3.1: Role of Microbes and Biofilms in Radionuclide Transport. Microbes are known to generate chemical compounds which are released to the surrounding environment or are used to create biofilms. Many of these exuded chemicals may influence the pH of the local environment, complex certain metals, or cause chemical reactions (e.g., redox chemistry) to occur. Biofilms and some microbes are also known to sequester and, often, accumulate certain chemical species, including radionuclides like Cs, Sr, actinides and lanthanides. This task will be a natural extension of Task 2 and employ many of the same methods to examine the surface and interfacial chemistry of microbes, biofilms, mineral surfaces and contaminant species in order to elucidate the mechanisms of biofilm mediated radionuclide transport.

Subtask 3.2: Chemical Interaction of Radionuclides and Metal Contaminants with the Mineral and Other Surfaces. Basic surface chemical mechanisms are related to all of the above mentioned tasks. In many cases, knowing how a chemical species interacts with specific surfaces is very important in determining the fate of that species or in the ease with which it can be cleaned up. This task will utilize analytical tools similar to those developed for many of the other tasks to study the direct interaction of contaminants with relevant surfaces under relevant conditions.

FY 1998 Technical Accomplishments

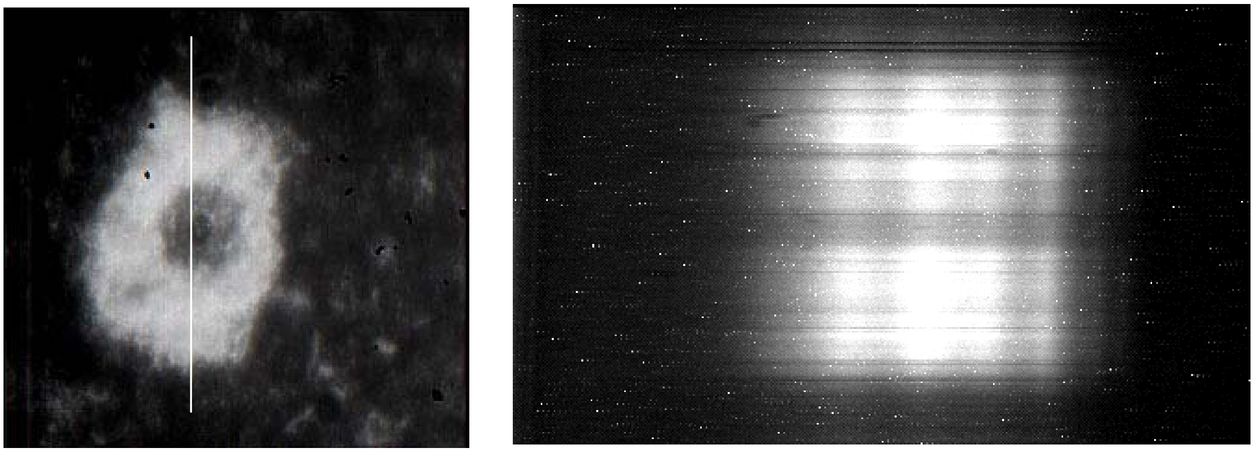
All of the FY-98 milestones as described in the scope and work package documentation were completed. Specific technical accomplishments for the tasks identified in the scope are described below.

Task 1. Analytical Developments

Instrumentation. During FY-98, a SPM with a wide range of capabilities, including NSOM, was purchased and installed (the Aurora and Explorer models from Topometrix Corp.) at the INEEL. Because this instrument was not installed until rather late in the year (August), work with this instrument is just beginning. Only noncontact AFM images of bacteria on membrane filters have been obtained thus far. However, to get this work started, Dr. Patricia Maurice at Kent State University was been enlisted to aid with method development using TMAFM to observe bacteria attached to iron oxide surfaces and the development of biofilms on these surfaces. Preliminary results from this collaboration will be discussed later as they were directly related to the work with iron-reducing bacteria (Subtask 2.1). Future work in our laboratory will focus upon the applications of NSOM since it can provide many similar advantages to the spectroscopic applications discussed below, but at a spatial resolution that is potentially reduced by a factor of five.

Fluorescence spectra are naturally somewhat broad and therefore a high probability exists for spectral overlaps to occur. Conventional microscopes are limited in their application to the use of chemical probes because they rely on the use of one or two optical filters for wavelength discrimination. Because of the limitations imposed by the many spectral interferences and wide bandpass filters, quantitative analysis with fluorescence microscopy is difficult. A better method for getting around interference problems is to use a more selective optical filter that will provide much more information. Such a filter would actually be a spectrograph that collects spatially resolved spectroscopic information at multiple wavelengths. Such data can be processed using a multitude of available spectroscopic routines to classify objects in the image, remove interferences, and provide more accurate quantitative information.

In order to collect such spatially resolved spectroscopic information, a Nikon Eclipse E600 optical microscope with epifluorescence was purchased and subsequently equipped with a PARISS microspectroscopic attachment. The microscope also arrived late in the year (August) and was just recently set up. Figures 1 and 2 are a demonstration of the type of data that can be obtained with this instrumentation. Figure 1 is a fluorescence image of a clump of acridine orange stained *S. alga* cells with some individual cells visible and the corresponding fluorescence spectroscopic image of the showing all of the spectra along the line of the original image. Figure 2 shows an average spectrum from the spectral image in Figure 1 and a spectrum of a mass of green cells on the same slide. Exitation was from a mercury vapor lamp filtered through a bandpass filter at 485 ± 20 nm. The fluorescence >550 nm passes through a dichroic mirror to the detection optics. Acridine orange interacts with DNA and RNA by intercalation or by electrostatic attractions. With DNA, a green fluorescent is obtained with a maximum of ~525 nm and with RNA, the fluorescence is more red with a maximum of near 650 nm. From the spectrum of the green mass, one can note a small amount of the red fluorescence with RNA, some of the green fluoresence with DNA and some fluorescence from an unknown compound(s). The green fluorescence photobleaches rapidly, however, the changes in the spectral properties have not been tracked. It can be seen in Figure 2 that the green fluorescence could significantly affect quantitative data much of the spectral range of the spectrum of RNA intercalated acridine orange. Future work will include application of some common chemometric tools to process the spectral images in order to eliminate interferences and to be able to quantitatively track fluorescent compounds indicative of specific chemical properties.



Group of cells

Spectrum vector image

Figure 1. Microscopic image (left) of a group of cells from a slide prepared from a culture of Shewanella alga stained with acridine orange and the corresponding spectral image (right) of a slice through the image.

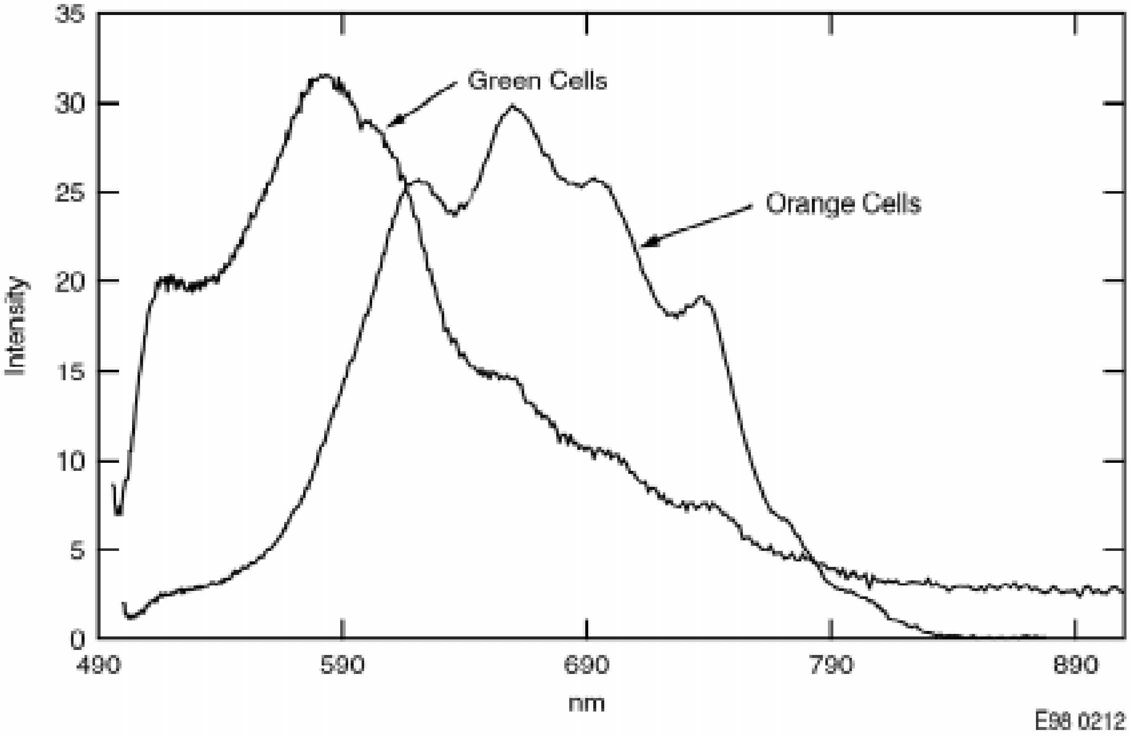


Figure 2. Average spectrum of acridine orange stained *S. alga* cells from Figure 1 and an average spectrum from cells appearing green on the same slide.

Fluorescent probes for chemical activity. Many of the interactions of microbes with surfaces may occur because of localized chemical environments. The local chemical environments may be related to membrane potential or pH, for example. Formation of biofilms and other interfacial zones between the bacterium and the surface may form zones with a specific set of conditions that alters the surface. To probe this, procedures are being developed to probe pH and redox potential using fluorescent indicators such as SNARF-1 and BCECF. These indicators are available commercially but have been used primarily in research involving eucaryotic cells or toxicological studies of bacteria. Following is a preliminary procedure for determining intracellular pH with a SNARF indicator.

Shewanella alga was grown to the late log phase in tryptic soy broth and harvested by centrifugation. Cells were washed in phosphate buffer to remove residual growth medium and then resuspended in buffer. Carboxy SNARF-1, which is loaded into cells as its cell permeant acetoxymethyl (AM) ester, was prepared in dimethylsulfoxide and added to the washed cell suspension at a final concentration of 50 μM. The cells were incubated for one hour to allow the indicator to localize in the cytoplasm and then washed in buffer to remove unhydrolyzed AM esters. A small aliquot of the loaded cell suspension was diluted in deionized water and collected onto a polycarbonate filter (0.2 μm pore size). The filter was then mounted on a slide for examination by fluorescence and fluorescence/confocal microscopy/spectroscopy.

Calibration curves for the indicator-loaded cells were obtained by using the ionophore nigericin to exchange intracellular K^+ for extracellular H^+. A 40 μL aliquot of the loaded cell suspension was added to a series of potassium phosphate buffers at pH 4.3, 6.0, 6.4, 7.0, 7.4, 7.6, 8.0, and 8.9. Nigericin was added to each solution at a final concentration of approximately 10 μM. The emission intensity of each solution was then measured at excitation wavelengths of 488, 514 and 534 nm over a spectra range of 500–700 nm using a spectrofluorometer. The ratio of the emission intensities at 590 nm and 640 nm was then calculated for each pH value and used to construct a calibration curve. Figure 3 is an example of the normalized fluorescence spectra obtained after excitation at 488 ± 10 nm and a resultant calibration curve plotting pH vs. response where

$$\text{Response} = \text{Log}\left[K_a\left(\frac{R - R_b}{R_a - R}\right) * \frac{F_{b(\lambda 2)}}{F_{a(\lambda 2)}}\right]$$

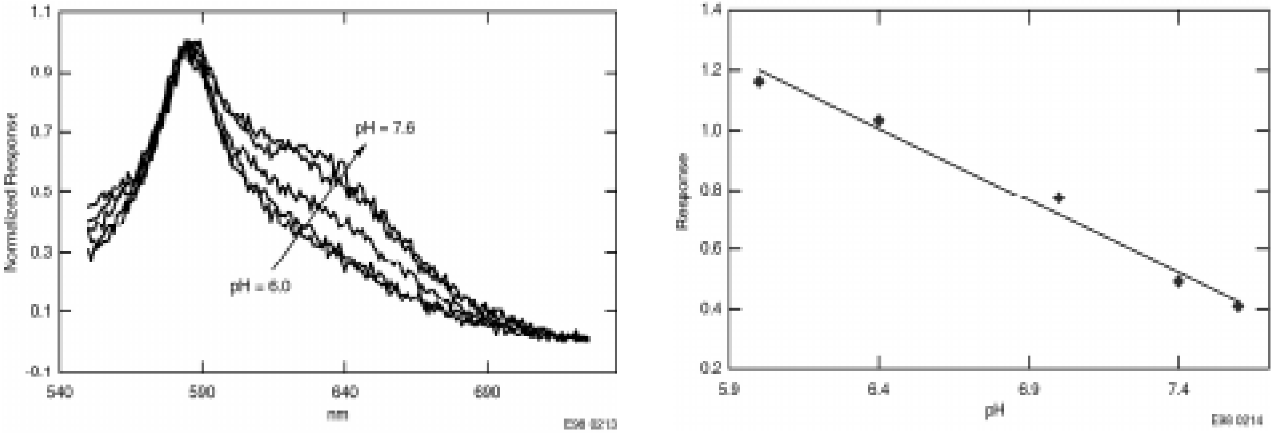


Figure 3. Normalized fluorescence spectra of SNARF-1 AM loaded into *Shewanella alga* cells suspended in a buffer and the resulting calibration. Exitation at 488 nm with a bandpass of ~20 nm.

and R is the ratio of fluorescence intensities $F_{\lambda 1}/F_{\lambda 2}$, R_a and R_b are the fluorescent intensity ratios at the acidic and basic endpoints of the titration, respectively, and $F_{b(\lambda 2)}/F_{a(\lambda 2)}$ is a normalization factor necessary if the pH independent isobestic point is not used as one of the wavelengths. While these spectra have a relatively low signal-to-noise ratio, they are still quantitative and can be significantly improved by optimization of the instrumental parameters. Similar curves to those in Figure 3 can be obtained using the confocal microscope. The major problem with the analysis is associated with the leakage of the indicator from the cells.

Raman microspectroscopy. Raman microspectroscopy has many of the same advantages as the fluorescence microspectroscopy discussed above. However, the kinds of chemical information obtained can be quite different. Raman spectroscopy can be used to determine chemical information ranging from molecular identification to structure to simple functional group analysis.

To assess the potential value of a new design of Raman microspectroscopy instruments that are now available,[5] a small service contract with ChemIcon, Inc., was placed for time on one of their instruments. This instrument essentially consists of a microscope with infinity optics, exitation at 532 nm with a diode-pumped Nd:YAG solid state laser that is delivered to the microscope through a fiber optic, a liquid crystal tunable filter (LCTF) for wavelength resolution (to ~8 cm^{-1} bandwidth) of the scattered light, and an intensified CCD camera to collect the images. The system also has a separate fiber optically coupled spectrograph and CCD detector to collect Raman spectra from the entire field of view. While the data collected at ChemIcon has not yet been fully evaluated, some promise for the technique has been noted.

Figure 4 is a series of spectroscopic images that were collected from a hematite disk having some bright orange inclusions. A total of 19 Raman images were collected from 1,222 to 1,495 cm^{-1}. The images are a reflection of the direct Raman spectroscopy of the hematite disks. The black hematite disks have a broad peak around ~1,320 cm^{-1} (1,400–1,240 cm^{-1}) that is considerably sharper for the bright orange features. Images at 1,299 and 1,330 cm^{-1} show little evidence of the feature seen in the 1,315 cm^{-1} image. The orange colored body fades under the intensity of the laser light, however, the spectral peak at ~1,320 cm^{-1} remains narrow. This is likely a highly crystalline form of hydrated hematite. Although Raman spectroscopy is generally considered insensitive, the microspectroscopic technique may prove to be useful for mapping changes in chemical mineralogy at fairly high spatial resolution. Basalt

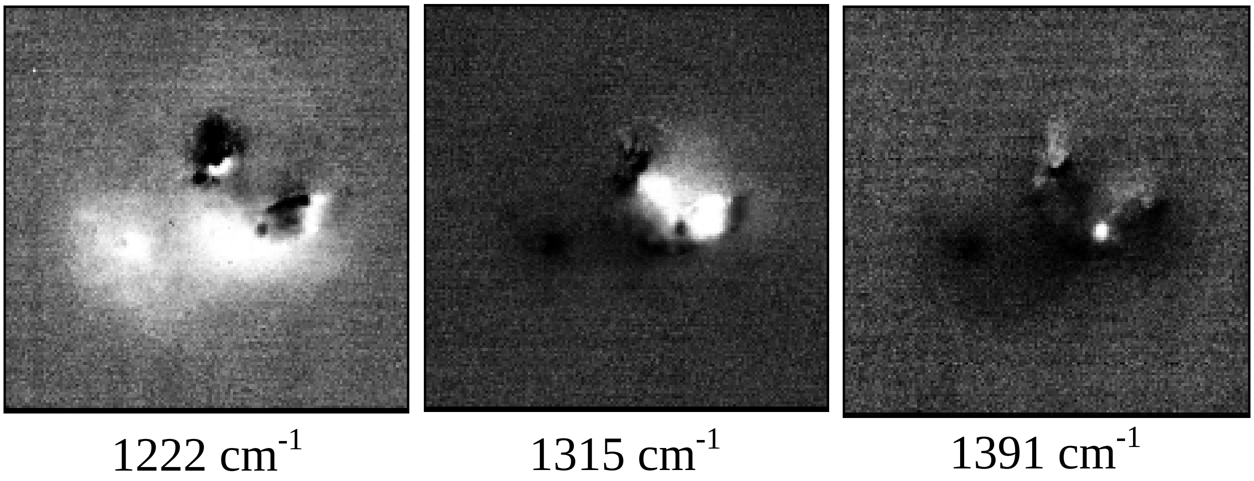

1222 cm^{-1} 1315 cm^{-1} 1391 cm^{-1}

Figure 4. Raman microspectroscopic images of a bright orange feature found on a hematite disk.

composition is highly variable on a microscopic level and this technique may prove valuable for determining microscopic changes in the mineral phases. It may also be possible to obtain images or organic distributions by working with the CH stretching region. Initial attempts looked promising but the time necessary for optimization was not available.

Task 2. Biological/Geochemical Methods/Systems

Subtask 2.1: Fe-reducing Bacteria. The cycling of iron in the subsurface environment is important because it influences the redox properties of the system. Bacterial reduction of iron oxides can influence transport and fate of many contaminants. Reduced iron may enhance the natural attenuation of chlorinated solvents or mobilize other contaminants by reduction. Several issues are associated with reduction of iron oxides by bacteria. Among these are that the iron-reducing bacteria must interact directly with the insoluble iron oxides to utilize them as terminal electron acceptors. The how and why of this interaction between the bacterium and the iron oxide surface remains largely a mystery. The iron reduction of iron by bacteria can likely be explained by electrochemistry, however, the nature of the “enzymes” that the bacteria utilize to reduce are either not known or poorly understood.

This subtask can be broken down further to three objectives. The first of these would be the preparation of iron oxide surfaces suitable for use in the experiments designed to determine the nature of their interaction of iron-reducing bacteria. The second is to determine the extent of the interaction of an iron-reducing bacterium with the prepared surface under various conditions. The third is to determine the nature of the chemicals responsible for iron reduction.

Ideal surfaces and materials for use in surface studies are hard to find. Since bacteria to be studied are frequently in the 1 µm or less range, the surface should not have features with dimensions greater than ~50 nm so that the bacteria readily stand out from the background. Sputtering of the minerals onto an already smooth surface like glass appears attractive since, by controlling the conditions carefully, it should be possible to lay down mineral layers of precise morphology and thickness. Attempts have been underway to prepare sputtering targets of iron oxides so that such sputtered surfaces can be prepared in the future. To prepare a hematite target, Fe_2O_3 powder is cold pressed at 5,000 psig and then sintered at 1,300°C in air. The composition of resulting hematite disks has been confirmed with x-ray diffraction. Upon examination, it was determined that these disks could be polished with 3 µm diamond paste to prepare surfaces adequate for AFM and the initial experimental studies. A set of polished hematite disks was prepared for use. Attempts have also been made to make similar sputtering target pellets of other iron oxides (wűstite, FeO and magnetite, Fe_3O_4) by varying the starting material, sintering temperature and gas composition in the sintering furnace. The x-ray diffraction results for these samples are still pending.

Optical microscopy is not sufficient to determine how µm-sized bacteria interact with a surface. Standard surface analysis techniques can only be applied under high vacuum conditions and the bacteria/surface interaction cannot be observed in situ. The newer SPM techniques can be applied to samples at ambient conditions and even directly in aqueous environments. The spatial resolution and the ambient condition make SPM, and more specifically Tapping Mode or Noncontact AFM ideally suited for visualizing the interaction of bacteria with surfaces and the development of attachment features, biofilms, etc.

Experiments have been conducted to examine the interaction of the iron-reducing bacterium *S. alga* with the hematite target pellets prepared as described previously. Bacteria are incubated with the hematite pellets under areorbic and anaerobic in TSB media. TSB media was selected for the initial work because the bacteria grow well and lengthy experiments would not be required to observe surface interactions.

Figure 5 contains two TMAFM amplitude mode images from the initial experiments. In this experiment, the hematite pellet surface was examined after incubation in a culture of *S. alga* for two days under anaerobic conditions. The pellets were rinsed with a gentle stream of DI water and then dried at 100°C. Several features are notable in the images including the presence of flagella indicating that some of these bacteria were motile not long before the pellet was removed from the medium. The flagellated bacteria also tend to have relatively large granules distributed on their surface while the other bacteria have only small granules on their surfaces. These granules are associated with the bacterial bodies since they are not evident on the hematite surface which shows only the polishing marks. Close examination of the upper portion of the image on the right shows the beginning of web-like features extending to the pellet surface. The right hand image also shows a couple of larger bodies with collapsed centers. The nature of the granules is not known, however they have also been observed in the early experiments by scanning electron microscopy.

When the experiments were repeated, it was observed that rinsing with the gentle stream of water was probably too rigorous as many of the cells were washed away or torn off leaving only remnants behind. Rinsing away the growth medium is now performed by placing a drop of deionized water on the pellet and wicking it away with a absorbant tissue. This is repeated five times. Then the pellet is dried at ambient temperatures. Figure 6 contains a height and corresponding amplitude mode image of a similar anaerobic incubation of a hematite pellet with *S. alga* for two days. Note that the granules seen in Figure 5 are absent. The source of the granules is still unknown but this may suggest that it may have been an artifact of the sample preparation. Close examination of the bodies in Figure 6 show that many of these bacteria have flagella indicating that they are recently from a motile phase. The bodies also seem noticeably longer with very distinct surface depressions in a somewhat regular pattern.

At this point, the appropriate methodologies for preparing these samples for AFM analysis are still under development. The experiments have necessarily been aborted in several cases due to contamination. However, the images and experience obtained so far have been quite good and show promise for visualizing the surface interactions of these microbes with the surface. Ultimately, AFM images will obtained with living systems in an aqueous medium.

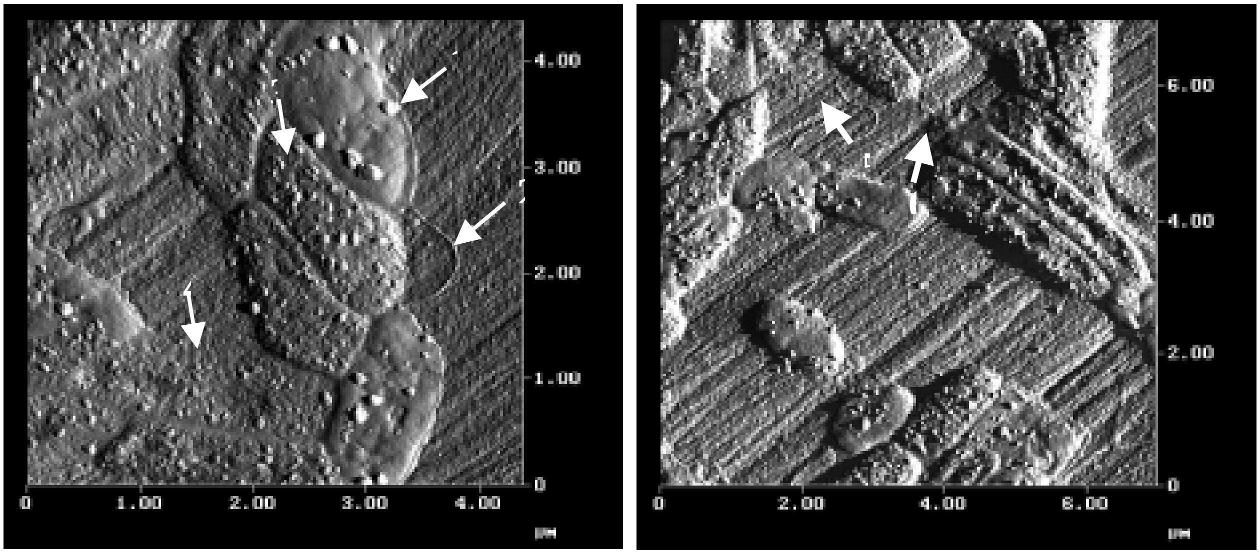
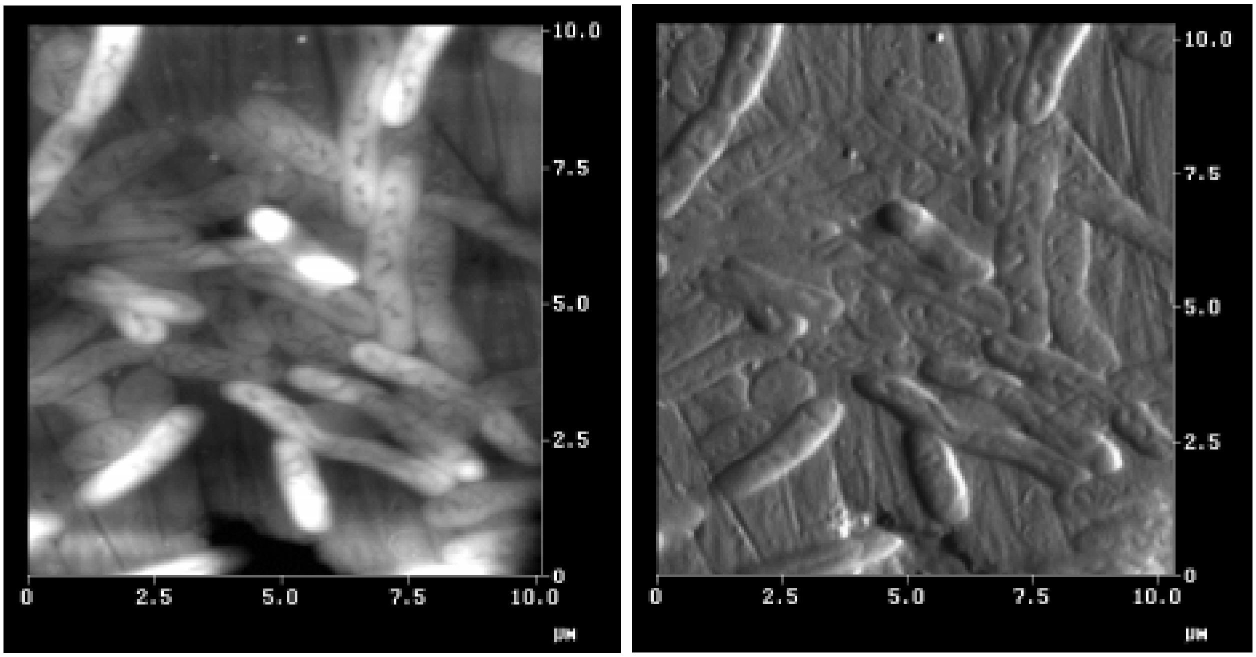


Figure 5. TMAFM amplitude mode images of hematite pellet surfaces after incubation with *S. alga* for 48 hours. Samples were rinsed with a gentle stream of deionized water and dried at 100°C.



Height Image

Amplitude Image

Figure 6. TMAFM images of bacteria after incubation for two days under anaerobic conditions.

Bacterial cytochromes are frequently identified as the "enzyme" responsible for iron-reduction.[6] These cytochromes are usually membrane bound entities, therefore, to isolate and identify these proteins the cells must be broken and the resulting fractionates purified. For method development purposes as a means of assessing our developed methods, membrane fractions were initially prepared using *Escherichia coli*. The respiratory chain of this microbe has been studied extensively and the cytochromes present under various growth conditions are well documented.

To prepare the fractions, *E. coli* was grown overnight at 30°C in 1 L of tryptic soy broth under aerobic conditions. The cells were harvested by centrifugation at 12,000 x g and 4°C for 20 minutes. To remove residual growth medium, the cell pellet was washed in 100 mL of phosphate buffer (pH 7.0), centrifuged (12,000 x g, 20 min., 4°C), and then resuspended in 0.05 M KH_2PO_4/0.15 M Na_2SO_4 solution. Cells were broken by two passages in a French pressure cell maintained at approximately 20,000 psi. Whole cells and debris were removed by centrifuging the suspension three times at 5,000 x g and 4°C for 10 minutes. The resulting supernatant was purified and concentrated by ultrafiltration at 4°C using a Biomax-100 filter and Amicon centriprep-50, centriprep-30, and centriprep-10 ultramicrofiltration membrane filters. These filters produce molecular weight fractions ranging between 0–100K, 0–50K, 0–30K, 0–10K, respectively.

The molecular weight fractions are then separated using gel permeation chromatography (GPC). Macrosphere GPC columns with pore sizes of 60 Å, 100 Å, and 300 Å were evaluated for their ability to separate cytochromes and other proteins present in the bacterial membrane fractions. The molecular weight exclusion limits of these columns were 250–8,000, 2,500–350,000 and 7,500–1,200,000, respectively. Commercially prepared cytochrome C (MW 12,300), bovine serum albumin (MW 66,200), beta lactoglobulin (MW 18,400) and lysosyme (MW 14,400) were used as molecular weight standards at concentrations between 500 and 1,000 ppm. Separation of the proteins by the individual columns and various combinations of joined columns were assessed. The HPLC system used for the analysis consisted of a Waters Model 600 controller, Model 717 autosampler, and Model 991 photodiode array detector. The mobile phase was a buffer consisting of 0.05 M KH_2PO_4 and 0.15 M Na_2SO_4 (pH 7.0) flowing at 0.3 mL/min. Reconstructed chromatograms at 220, 280, 420, and 556 nm were evaluated to identify possible cytochrome compounds. The 420 and 556 nm chromatograms are at characteristic wavelengths for determining cytochrome activity.

Unexpectedly, the 100 Å and 300 Å pore size columns were found to separate the proteins more efficiently than the smaller 60 Å column. The 60 Å columns demonstrated an uncharacteristic elution profile that did not appear to be related to solely molecular weight or size. Joining a 300 Å and a 100 Å column and using a 20 μL sample size resulted in good resolution of cytochrome C, beta lactoglobulin, and serum bovine albumin.

Figure 7 is a sample of the separation of the 0–10K Dalton extract fraction using the 300 Å and 100 Å columns in combination. All of the compounds appear to have a molecular weight of ~13K Daltons or less. The chromatograms plotted at 420 and 556 nm have some significant peaks that are likely cytochrome-type compounds or other compounds with a heme center. The negative peak in these two chromatograms is probably related to a fluorescent compound coeluting with the other proteins. This will be verified by examination of the entire UV-Vis absorption spectrum and fractions may be collected for fluorescence spectroscopy. Although these procedures have not been refined at this point, this methodology appears promising for isolating and identifying cell fractions containing possible iron-reducing compounds based on molecular weight. Future work will expand the application of the developed procedures to other bacteria species and will include methods for determining the electrochemical properties of the cell fractions since they will directly target compounds likely to have iron-reducing potential.

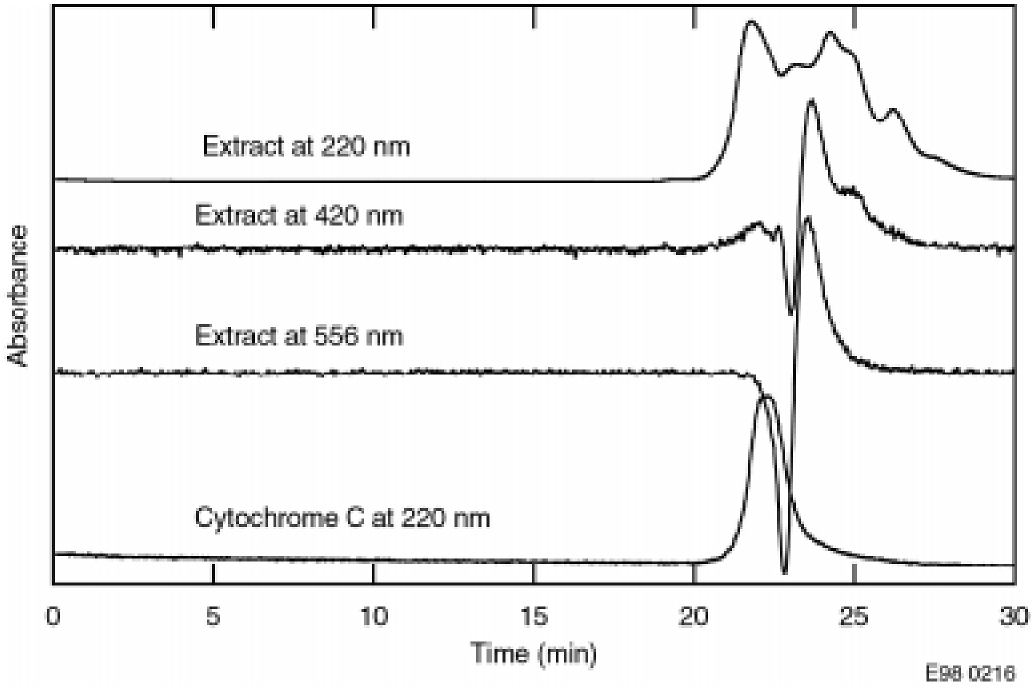


Figure 7. GPC separation and detection of a 10000 Dalton fraction from a culture of *E coli* and a cytohrome C.

Subtask 2.2: Interaction of TCE Degrading Bacteria with Mineral Surfaces. Initial experiments were conducted with Olivine and Labradorite minerals ground and sieved to average grain size of 50 um. Olivine was exposed 24 hrs to R2A growth media and B. cepacia, shaken at 30°C to evaluate the use of AO staining and confocal microscopy for observing cells on the mineral surfaces. Cells from solution phase (planktonic) were filtered over sterile mineral grains and stained and compared to suspended mineral grains that had been incubated with the bacteria, filtered and stained (no rinsing of the suspended mineral grains). Cells stained well and were easily observed, however the crystalline nature of olivine made differentiation of cells actually attached to the mineral difficult and no differences were observed between samples that had cell suspension filter over the sterile mineral and samples where incubated mineral was directly filtered and stained. A gentle rinsing procedure was evaluated using labradorite mineral inoculated with P. putida in R2A growth media and incubated on a shaker at 30°C for five days. Mineral grains were removed from solution and gently washed with three successive rinses of fresh, sterile R2A media followed by low speed centrifuging for 30 second intervals. The mineral grains were filtered and stained with AO and observed with the confocal microscope. Following this gentle rinsing procedure, essentially no cells were observed by confocal microscopy directly on the mineral surfaces that had been exposed to bacterial cultures. In both the labradorite and olivine exposed cultures, planktonic cells stained with A.O. were easily observed with confocal microscopy. Planktonic cells that were exposed to mineral were observed to be smaller in size and demonstrated less motility than cells from original cultures. Planktonic cells exposed to mineral and transferred to solid media plates demonstrated greater "slime production" than original cultures.

The following hypotheses were generated for further investigation:

- Slime production is increased in the presence of mineral surfaces and therefore preparation techniques for staining and observation must accommodate the possibility that physical stress may detach the slime and cells prior to microscopic observation

- Grain size effects attachment/detachment processes and subsequent observation of cells on mineral surface

- Bacterial cells are smaller when grown in the presence of minerals due to a surface interaction

- Bacterial cells are smaller when grown in the presence of minerals due to inhibitory effects of mineral components which leach into solution

- Bacterial cells promote the leaching of inhibitory compounds from minerals.

Mineral leaching experiments with bacterial growth media were conducted. Labradorite mineral, ground and sieved to 50 um, was incubated in R2A growth media both with and without addition of bacteria (*P. putida*). Supernatant was filtered and analyzed by ICP for heavy metals. No evidence of heavy metal leaching that could account for bacterial morphology was found. Of the heavy metals analyzed, Al, Cr, Cu, Fe, Mn, Ni, Sr, and Zn , none exhibited concentrations that should be considered inhibitory to bacterial growth or activity. All concentrations were less than 1 µg/ml. No evidence that bacteria promote the leaching of heavy metals from minerals was found. Significant differences were observed between the biotic treatment and the abiotic control for three metals only, Al, Mn, and Zn, and the concentration was actually greater for the abiotic control compared to the biotic treatment in all three cases. This preliminary evidence suggests that a surface phenomenon may be responsible for the morphology change exhibited by the bacterial cells (size and motility).

Experiments were designed and initiated to test the hypothesis that presence of the mineral surface is necessary to induce bacterial cell morphology changes. Olivine and labradorite minerals ground to 50 um size were incubated with sterile R2A growth media. Supernatant will be centrifuged and filtered. Fresh cultures of *P. putida* and *B. cepacia* will be used and inoculated into aliquots of the filtered supernatant and into fresh, sterile R2A media. Samples will be taken at regular intervals and examined with direct microscopy and image analysis to obtain growth curves (cell density vs. time) and size distributions with time.

Experiments were designed to evaluate the effects of surface area/volume on bacterial growth and attachment. Rinsing techniques are being developed and evaluated to determine the effects of rinsing technique on observed bacterial attachment to mineral surfaces using confocal microscopy. Cell growth and attachment will be observed on labradorite mineral that has been cut into larger pieces approx. 2 mm length X 2 mm width and 1 mm thick, and compared to growth on finely ground mineral (50 um). Both *B. cepacia* and *P. putida* bacterial treatments are planned. Cells will be inoculated into R2A media containing the same mass of mineral either in chunk or powder form. A biotic control without mineral added will be used. Growth curves and size distribution of planktonic cells will be done. Aliquots of suspended mineral will be removed, rinsed, and stained with AO for confocal microscopic examination. Two rinsing regimens will be evaluated. Gentle rinsing with sterile growth media and low speed centrifugation, and a wicking technique being evaluated in Subtask 1 will be compared.

These preliminary experiments conducted with bacteria capable of co-metabolism of chlorinated compounds in the presence of minerals commonly found in basalt indicate that the minerals olivine and labradorite appear to influence bacterial morphology and activity, resulting in reduced cell size, decreased mobility, and increased slime production. Early indications are that these effects may be the result of surface interactions and not the result of change in solution chemistry due to the mineral components. Conclusive experiments to evaluate the need for the mineral surface to be present to induce these changes in cell morphology are underway. Preparation and staining techniques are being developed to observe attachment of bacteria to the mineral surfaces. Effect of mineral particle size on bacterial attachment is being examined. Use of confocal microscopy for observing bacteria and mineral surfaces has been successful.

Task 3: Factors Influencing Chemical Transport

This task and, in particular, the subtasks were selected because they have relevance to DOE-EM issues but also because they are highly complimentary to all of the other tasks. No technical progress has been made on these tasks in FY-98, however, FY-99 plans are under development.

Summary

A program has been defined and initiated that is focused upon the application and development of novel analytical methodologies to spatially determine relevant chemical environments that have an effect on or are effected by environmental surfaces. Such environments may be related to chemical surface heterogeneity and/or microbiological action. Focus is being placed on techniques and methods that utilize molecular spectroscopies and microscopy so that the systems under study can be ultimately examined under ambient conditions. Fluorescence microspectroscopy can provide highly spatially resolved information on local chemical environments through the application of fluorescent probes that a specific for such parameters as pH, redox potential, or ion complexation. Scanning probe techniques are being investigated as a means of providing highly spatially resolved morphological information that can be related to the local chemical environments. In particular, NSOM will provide very high spatial resolution fluorescence microspectroscopy than can be directly related to surface structure. Development of analytical techniques and methods is only of importance if they can applied to real problems to provide critical pieces of information. For that reason, tasks to study the mechanisms used by iron-reducing bacteria to reduce iron from highly insoluble iron oxides and how the nature of the interaction of microbes with mineral surfaces changes in the presence of a contaminant have been initiated.

Technical progress has been primarily in the areas associated with the development of AFM techniques to study interaction of microbes with mineral surfaces specifically as applied to the interaction of iron-reducing bacteria with the surfaces of insoluble iron oxides. Progress has also been made in the application of fluorescent probes to study the microchemical environments found inside and surrounding bacterial cells. Fluorescence microspectroscopy, confocal microscopy and NSOM will ultimately be used to study the influence of microbes on the surfaces they come in contact with. Progress has also been made in the development of techniques to determine the active iron-reducing "enzymes" used be various bacterial species in iron reduction.

Preliminary experiments have also been conducted with bacteria capable of co-metabolism of chlorinated compounds in the presence of minerals commonly found in basalt. These experiments indicate that the minerals olivine and labradorite appear to have an influence on bacterial morphology and activity. Early indications are that these effects may be the result of surface interactions of the microbes with the mineral and not the result of change in solution chemistry due to the mineral components. Preparation and staining techniques are being developed to observe attachment of bacteria to the mineral surfaces. Effect of mineral particle size on bacterial attachment is being examined. Use of confocal microscopy for observing bacteria and mineral surfaces has been successful.

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REACTIVE TRANSPORT IN VARIABLY SATURATED HETEROGENEOUS MEDIA

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Scope and Objectives

Water quality has deteriorated in recent decades in many areas throughout the United States. This has threatened water supplies which is particularly worrisome because the demand for water keeps increasing.

The objective of this task is to increase understanding of how contamination migrates through the vadose zone, which is the region between the earth's surface and the underlying water table.

Four tasks were established for FY 1998:

1. Up-scaling of Geochemical Heterogeneity.
2. Propagation of Geochemical Environment in the Vadose Zone
3. Integrated Vadose Zone Characterization
4. Enhanced Computational Methods

Technical Accomplishments

Background

Throughout arid portions of the world, as exemplified by the Western United States, water quantity and quality are major concerns to the general population, agricultural communities, mining and energy resource interests, and local and national governments. Water supplies are becoming critically impacted as population and water demands increase. In many locations, water supplies have been contaminated either by accident or as a result of past waste-disposal practices. For example, within the United States, activities of the U.S. Department of Energy (DOE) have resulted in the contamination of large tracts of land with complex mixtures of radionuclides and other contaminants. Much of this contamination results from the migration of wastes disposed of at the land surface into the region between the surface and underlying aquifer. Other activities that occur in and may result in contamination of the vadose zone include the following:

- Disposal of municipal and hazardous waste in landfills
- Suburban septic systems
- Mining and milling of ores
- Production and refining of petroleum products
- Application of agricultural chemicals (e.g., fertilizers, pesticides, and herbicides) to crops.

Although the vadose zone is often relied on as the primary protective barrier to prevent groundwater contamination, it is often the conduit for the transport of contamination from the surface to subsurface water supplies. However, our current understanding of the movement and transformation of contaminants is not adequate to accurately predict their behavior in the vadose zone. For example, simplistic chemical characterizations and supporting modeling of the behavior of actinides and other radionuclides in the vadose zone suggest that these contaminants are immobile. However, at some locations [e.g., the INEEL Radioactive Waste Management Complex (RWMC) and the Hanford Tank Farms], actinides and other radionuclides have migrated hundreds of feet through the vadose zone and are influenced by poorly understood physical, chemical, and biological processes. Because centuries of human activities have led to water use and disposal practices that are not environmentally sustainable, new coordinated research and technology development activities are needed for improved and sustainable stewardship of the vadose zone.

The Idaho National Engineering and Environmental Laboratory (INEEL) through the Core Capabilities and Technical Enhancement program embarked on a three-year project with the objectives of developing a better understanding of the movement and transformation of reactive constituents in heterogeneous, variably saturated subsurface media (e.g., vadose zone) and parlaying this better understanding into improved estimates of the fate and mobility of reactive constituents in the vadose zone. The Core Capabilities and Technical Enhancement program is organized into six theme areas. This project along with “Advanced Strategies for Probing Structure and Reactivity at the Top Monolayer (fundamental analytical surface chemistry),” “Biochemical and Geochemical Reactions on Environmental Surfaces (interfacial processes research),” and “Transport Phenomena in Geologic Porous Media (experimental-based evaluation of biogeochemical processes in porous media)” comprise the Chemistry of Environmental Surfaces theme area. The specific goals of this project are to

- Build upon existing INEEL expertise in vadose zone processes through laboratory and field investigations and by developing mechanistically oriented models that can adequately simulate the complex behavior of contaminants in the vadose zone

- Identify and hire a senior level scientist or engineer with a national reputation in the simulation of contaminant behavior in the vadose zone

- Provide educational opportunities through post-doctoral research fellowships to recently graduated scientist and engineers working on vadose zone problems

- Transfer the expertise and models developed to DOE environmental remediation programs

- Identify derived use markets (e.g., agriculture, and mining) for the expertise and models developed.

Within the science and engineering community numerous disciplinary investigations exist relevant to understanding and modeling the behavior of contaminants in the vadose zone. However, the ability to predict 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 the transport, retention, and transformation of contaminants and other solutes (nutrients, electron acceptor/donors, etc.) to be accurately assessed. This framework must include

- A high degree of temporal resolution so that effects on contaminant transport and transformation of events such as snow melt can be evaluated

- A high degree of spatial resolution so that effects on contaminant transport and transformation of physical, chemical, and biological heterogeneities can be evaluated

- Appropriate coupling of the important biological, geochemical, and transport processes so that synergistic and antagonistic effects can be evaluated.

Theoretical derivations, experimental investigations, and field observation will be needed to fill key data or understanding gaps required to successfully develop improved predictive capabilities. As such, the scope of the project includes assessments of the scaling-up of processes in heterogeneous media, computer code development activities to simulate processes and couplings, and evaluations of how laboratory and field data and observations are incorporated into model parameterization. Specifically, three scientific choke points provide the focus for the four specific tasks of this project. Three of the tasks are hypothesis-driven and incorporate appropriate experiments and field measurements. The forth task is methods-oriented and crosscutting to the other three. The selection of these tasks was based on the results of a two-day INEEL-sponsored workshop held in Salt Lake City that involved project investigators and six vadose zone experts from the university research community. Specifically these tasks are:

Task 1: Up-scaling of Geochemical Heterogeneity. Biogeochemical processes occur at the pore-scale and involve interactions between advecting fluids, mineral surfaces, and microorganisms in a heterogeneous media. However, transport modeling is conducted at the scale of representative volumes. Often these representative volumes range from 10s to 100s of liters and require that the heterogeneity smaller than this be up-scaled and averaged. Although there has been much previous research on the up-scaling of physical heterogeneity, only limited research has been focused on the up-scaling of geochemical heterogeneity. In this task, high-resolution numerical modeling of small-scale heterogeneity will be conducted to assess how processes upscale and to determine if these heterogeneity result in anisotropy in geochemical properties. Select experiments on natural and synthetic heterogeneous systems will be conducted to validate up-scaling approaches. This research is being conducted in collaboration with Dr. George Yeh of Penn State University.

Task 2: Propagation of Geochemical Environment in the Vadose Zone. Unlike groundwater systems, in the vadose zone, both advection of water and/or gaseous diffusion/advection can transport volatile reactive species. This task will focus on the role of gaseous transport of inorganic carbon on the pH of advecting vadose zone waters. Inorganic carbon often controls pH in natural waters and can be transported by advective water movement [bicarbonate] or by gaseous diffusion or advection [carbon dioxide]. Ultimately, pH is one of the most important master variables in controlling reactive transport and other biogeochemical processes. Numerical simulations that include or exclude gaseous transport will be conducted and the effects on the reactive transport of a DOE-relevant actinide, uranium, will be assessed. Uranium will be used because it forms strong complexes with carbonate and occurs as either a cation or anion depending on the solution’s pH. This research is being conducted in collaboration with Dr. Donald Suarez of the U.S. Salinity Laboratory.

Task 3: Integrated Vadose Zone Characterization. A variety of characterization measurement techniques are available for the vadose zone. These measurements include point measurement (e.g., borehole vadose zone instruments), nonintrusive characterization (surface or cross-borehole geophysics), and processes measurements (e.g., reactive or conservative tracer breakthrough test). However, systematic approaches as to the distribution of measurement locations, number of measurements, and mixes of differing type of measurements that yield the maximum amount of information on the vadose zone are lacking. This task will focus on the integration of field vadose zone measurements and inverse modeling approaches to define more realistic representations of vadose zone heterogeneity that include estimates of property uncertainties and allow the design of improved vadose zone characterization strategies. This task will include a significant field component, as detailed field measurements will be required. We are developing a collaborative relationship with Dr. Jim Yeh (no relation to George Yeh) of the University of Arizona for this task.

Task 4: Enhanced Computational Methods. Numerical simulations of vadose zone processes require significant computational capabilities. The objective of this crosscutting task is to develop more efficient and optimized computational (e.g., parallel computing) approaches for the solution to the problems identified in the other three tasks. Where appropriate, this task will take advantage of other Core Capabilities and Technical Enhancement activities focused on advance computing.

The "Reactive Transport In Variably Saturated Heterogeneous Media" project was initiated in February 1998. A major activity of this fiscal year was to develop a technically credible science plan that guides the project activities. In association with the plan preparation, a workshop involving vadose zone experts from the university community was sponsored to evaluate and validate the science plan. The development of a science plan and the supporting workshop is based on the successful model used by the Subsurface Science Program of the Office of Biological and Environmental Research (OBER) to initiate interdisciplinary research projects. This model was used at the INEEL to develop the microbial ecology and intrinsic remediation Test Area North (TAN) research programs funded through OBER and the Environmental Management Science Program. The science plan and the results of the workshop are described in the project document entitled "Science and Modeling Plan for Reactive Transport in Variably Saturated Heterogeneous Media," completed in September 1998. Specific accomplishments for the scientific tasks (1 through 3 above) are given below.

FY 1998 Accomplishments

Up-Scaling of Geochemical Heterogeneity

The goal of this task is to explore the effects of variable saturation on the transport of contaminants in heterogeneous media. In particular the role that small-scale heterogeneities play in defining the anisotropy in media-reactive characteristics will be defined, so that generalized anisotropy relationship can be included in field-scale vadose zone modeling activities.

Depositional processes exert close controls on mineralogy, grain size, grain shape, sorting, and other sedimentalogical properties of sand bodies. Since the primary porosity (ϕ) of sand and sandstone bodies is a function of sedimentalogical variables, permeability (k) and ϕ should, in part, be functions of facies distribution. As an example, glacial till deposits are characterized by poor sorting with respect to size and shape and commonly consist of a fair amount of clay and silt, resulting in low k. Beach processes are more effective in removing silt to clay-sized grains and in size sorting grains, resulting in comparatively high k. Variations of these properties among depositional environments permit recognition of sediments from various parts of the depositional environment where different processes predominated during accumulation.

In addition to depositional processes, which produce primary sedimentary characteristics, postdepositional or secondary processes can alter the original hydrologic and chemical variability of sediment or rock units. Secondary processes can increase ϕ by the dissolution of calcite and feldspar grains in a particular section of strata, or decrease ϕ in another section by mineral precipitation. In addition, secondary processes can result in the formation of highly reactive mineral phases, such as hydrous metal oxides, that dominate the sorptive capacity and intensity of the sediments. Because these distributions are mechanistically controlled, it is expected that physical, hydrologic, and geochemical heterogeneities will be correlated. An example theoretical correlation between physical and geochemical heterogeneities for idealized porous media is discussed below.

Lerman (1979) reviews numerous relationships between *k*, ϕ, and grain size derived from earlier literature sources. Additional evaluations have been published recently by Sperry and Peirce (1995) and Alyamani and Sen (1993) and in a series of papers by Lake and others (Lake 1989, Panda and Lake, 1994, 1995, and Embid and Lake, 1996). Thompson et al. (1987) reviewed the physics and relationships among *k*, ϕ, and the microgeometry of sedimentary rocks. Smith et al. (1996, in prep) have derived a theoretical relationship between permeability and geochemical heterogeneities (as characterized by reactive surface area A_s)

$$A_S = \sqrt{\frac{\phi}{2\tau k}} \tag{1}$$

Where τ is the toruosity. Equation (1) links the reactive surface area to the media k and provides a theoretical basis for the expected correlation between heterogeneity in reactive properties and the heterogeneity in hydraulic properties for porous media. Taking the logarithm of Equation (1),

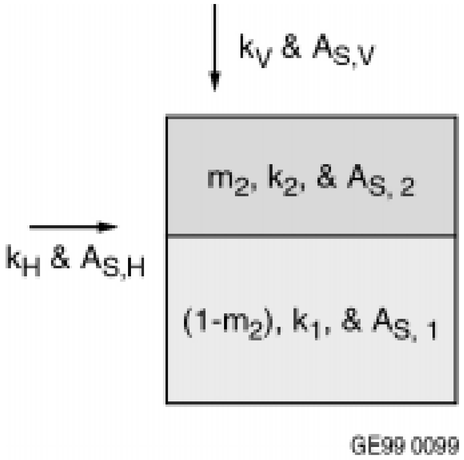
$$\ln A_S = 0.5\ln\phi - 0.5\ln 2\tau - 0.5\ln k \tag{2}$$

shows that ln A_S and ln k for unconsolidated sediments should be correlated with a slope of -0.5. In addition, both ϕ and τ should influence the relationship between A_S and k. In the simple case where both ϕ and τ are constant, Equation (2) reduces to a straight line. In the case where τ is constant, variations in ϕ should not significantly affect the expected relationship between A_S and k. However, the assumption of constant τ is probably valid for only limited ranges of ϕ. Panda and Lake (1994) discuss the importance of sediment sorting and packing on τ and indicate that τ is a power function of sorting. In addition, they suggest that small amounts of secondary minerals can significantly influence the value of τ. Because of potential variation of τ in an aquifer and of the difficulties in quantifying τ, the direct application of Equation (2) for developing correlated aquifer models is limited. However, it has been shown (Smith et al., 1996, Tompson et al., 1996, Smith et al., 1997 and in prep) that expressions of the form of Equation (2) can be used to describe the relationships between surface area-based biogeochemical reactivity and media permeability for monomineralic sediments and naturally occurring oxide coated sediments.

Equations (1) and (2) are derived for monomineralic packing of sand grains that are isotropic, that is the value of k is the same in all directions. This is the type of packing that is often strived for in column experiments and is usually obtainable only in repacked columns. Naturally occurring sedimentary aquifers exhibit anisotropic k (with $k_{horizontal} > k_{vertical}$) because of heterogeneities in packing and in grain size at scales smaller than the scale of interest for flow and transport. An example of the relationship between anisotropy in k and reactive surface area is presented below for a simple but important type of heterogeneity characteristic of horizontal banding.

A packet of sediments is defined with two layers of high (k_1) and low (k_2) permeability with relative thicknesses of 1-m_2 and m_2, respectively. The average (effective) horizontal permeability is given by the thickness-weighted arithmetic average of permeability and the effective vertical permeability is given by the thickness-weighted harmonic average of permeability.

$$k_H = k_1(1 - m_2) + k_2 m_2 \tag{3}$$



$$k_V = \frac{1}{\frac{1-m_2}{k_1} + \frac{m_2}{k_2}} \tag{4}$$

The ratio of the horizontal to vertical permeability is the anisotropy ratio, from which it is apparent that the anisotropy ratio will be greater than, or equal to, 1 regardless of the absolute values of k_1, k_2, and m_2.

$$\frac{k_H}{k_V} = \frac{\left(1 - m_2 + \frac{k_1}{k_2} m_2\right)\left(\frac{k_1}{k_2} + m_2 - \frac{k_1}{k_2} m_2\right)}{\frac{k_1}{k_2}} \tag{5}$$

Similar, although more complex, equations can be developed to describe the effective reactive surface area as a function of direction by using Equation (1) and appropriate volume and flux weighting for the bands. Effective surface area in the horizontal direction is calculated from the surface areas of the individual bands weighted by their relative thicknesses and fluxes and the effective surface area in the vertical direction is equivalent to the total surface area in the sediment packet.

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The anisotropy ratio for effective reactive surface area under conditions of uniform porosity and tortuosity, $A_{S,H}/A_{S,V}$ is given by:

$$\frac{A_{S,H}}{A_{S,V}} = \frac{m_2\left(\frac{k_1}{k_2} - \sqrt{\frac{k_1}{k_2}}\right) - \frac{k_1}{k_2}}{\left(1 - m_2 + m_2\sqrt{\frac{k_1}{k_2}}\right)\left(m_2\frac{k_1}{k_2} - m_2 - \frac{k_1}{k_2}\right)} \tag{8}$$

Inspection of Equations (5) and (8) reveal that both k_H/k_V and $A_{S,H}/A_{S,V}$ are independent of the absolute values of the permeability of the individual layers and that they depend only on the ratio of the permeability and on the relative thicknesses of the beds. Analysis of Equation (8) indicates that $A_{S,H}/A_{S,V}$ will always be less than or equal to 1 regardless of the absolute values of k_1, k_2, and m_2. This indicates that the effective surface area in the horizontal direction will always be less than in the vertical direction, illustrating the importance of the high permeability, low surface area bands in transmitting water. Figure 1 depicts the relationship between k_H/k_V and $A_{S,H}/A_{S,V}$ for several values of m_2. From this figure, $\ln k_H/k_V$ and $\ln A_{S,H}/A_{S,V}$ are inversely related (e.g., negative slope) with a slope that becomes more negative with increasing fraction of the low permeability bands. The implication to reactive transport is profound. Key is the concept that the effective reactive surface area and any property or process (e.g., K_d) that is related to reactive surface area will have directionally dependent values. The dependence is more pronounced in real systems. For example, the expressions presented above are for aquifer materials that are mineralogically homogeneous, with the contrast between bands being solely a function of particle size. In real systems the spatially variable distribution of reactive minerals such as hydrous ferric oxides tends to further reduce the permeability of low flow zones and tends to increase the reactive surface area in those low flow zones. As a result, the field-scale anisotropy in reactive surface area will be more pronounced than predicted based solely on grain size simply because of the nonuniform nature of the coatings.

These expressions illustrate that effective reactive surface area is expected to be an anisotropic property in a heterogeneous porous media. In addition, variable saturation conditions will influence the relationship between effective reactive surface area and permeability. Furthermore, if the moisture characteristic curves are significantly different for the two layers, the relative fluxes of water through layers 1 and 2 may reverse resulting in very low effective surface areas at high moisture contents and very high effective surface areas at low moisture contents. This implies that at high moisture contents only limited adsorption of contaminants will occur and that at low moisture contents significant contaminant adsorption will occur.

The use of effective reactive surface area as a scaling parameter that will link laboratory-scale studies with field scale-observations is being investigated. The mechanistic model HYDROGEOCHEM (Yeh and Salvage, 1997) is being used to conduct simulations of systems with small-scale heterogeneities as functions of the contrast in materials properties and water fluxes through the system. The results of these simulations are being treated as averaged materials response to define anisotropy relationship to use at larger scale. Currently, the commercially available version of HYDROGEOCHEM is strictly a transport code. However, G. Yeh has developed a fully coupled 2-D version (e.g., with respect to water flow) of the code, allowing the effects of biogeochemical reactions on the flow field to be evaluated.

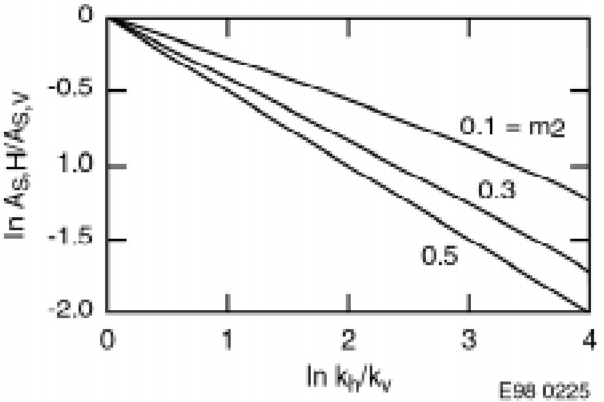

Figure 1. Anisotropic effective surface area and permeability for a two layer system.

Through this project, the INEEL plans to support Dr. Yeh in the development of the 3-D version of the coupled code in FY 1999.

The results of this task will be presented at the "Scientific Basis for Nuclear Waste Management" meeting held in conjunction with the Materials Research Society annual meeting in Boston in December 1998. In addition, a manuscript is also being prepared.

Propagation of Geochemical Environment in the Vadose Zone

The subsurface processes that control the fate and transport of contaminants within the vadose zone are functions of the geochemical environment. The geochemical environment and its propagation through the vadose zone reflect complex interaction among hydrologic, biological, and geochemical processes. However, performance assessment and risk assessment models typically do not address geochemical environment parameters that can have a significant impact on transport. The most important system variables for defining geochemical environments are pH and pe (or redox potential). Because arid vadose zone environments often have sufficient open pore space that diffusion of atmospheric oxygen maintains oxidizing conditions, variation of pH in the vadose zone is the focus of initial investigations. The objective of this task is to assess the processes and mechanisms controlling the propagation of pH in the vadose zone and incorporate these processes into a predictive reactive transport code. Future research will include assessing the evolution of redox potential in the vadose zone.

The partial pressure of CO_2 in the vadose zone, which is commonly 3 to 30 times the partial pressure in the atmosphere, in combination with calcite, a ubiquitous vadose zone mineral, is important in buffering the pH of vadose zone waters. The higher levels of CO_2 in the vadose zone are attributed to plant root respiration and microbial degradation of organic matter (Šimunek and Suarez 1993). Understanding the vadose zone carbon cycle is required to adequately access the partial pressure of CO_2 and estimate pH. However, in most geochemical computer codes, the partial pressure of carbon dioxide must be externally fixed (Parkhurst 1995; Allison et al. 1991; Serne et al. 1990; Kincaid et al. 1984) which precludes studying interactions between biological sources of carbon dioxide and inorganic sources of carbon dioxide. In addition, most codes can speciate metals or radionuclides given the pH, but cannot estimate the pH from underlying processes controlling the vadose zone carbon cycle. These limitations preclude a mechanistic assessment of how changes in system conditions (e.g., microbial activity) can affect other processes (radionuclide adsorption) in the vadose zone. Recently, a computer code (UNSATCHEM) has been developed that treats biological sources of carbon dioxide in the vadose zone explicitly (Šimunek and Suarez 1993; Suarez and Šimunek 1993, 1996, 1997) and permits an explicit calculation of carbon dioxide partial pressure in response to changes in the physical and geochemical state of the system. As part of this task, the UNSATCHEM code is being modified (in collaboration with its developer) to include more general geochemical algorithms and semi-empirical surface complexation adsorption submodel so that role of the vadose zone carbon cycle on the transport of radionuclides can be evaluated. Preliminary results considering only CO_2 production in one dimension are presented below and illustrate the importance of understanding the processes that control the production and movement of CO_2.

Figure 2a shows the estimated net rate of CO_2 production in the shallow vadose zone calculated using UNSATCHEM. The production rate is calculated at a uniform temperature of 20 ºC and represents the optimum production rate (summer growing season). As may be seen in this figure, most of the CO_2 is produced in the upper one to two meters of the vadose zone as a result of root respiration. Figure 2b shows the CO_2 partial pressure as functions of time and depth assuming the time invariant using the production rates given in Figure 2a. At land surface, the CO_2 concentration is fixed at atmospheric levels. In addition, the initial profile assumes that the vadose gas phase is the same as the atmospheric CO_2 partial pressure. At early times (5 days), the CO_2 concentration increases rapidly with depth reaching a

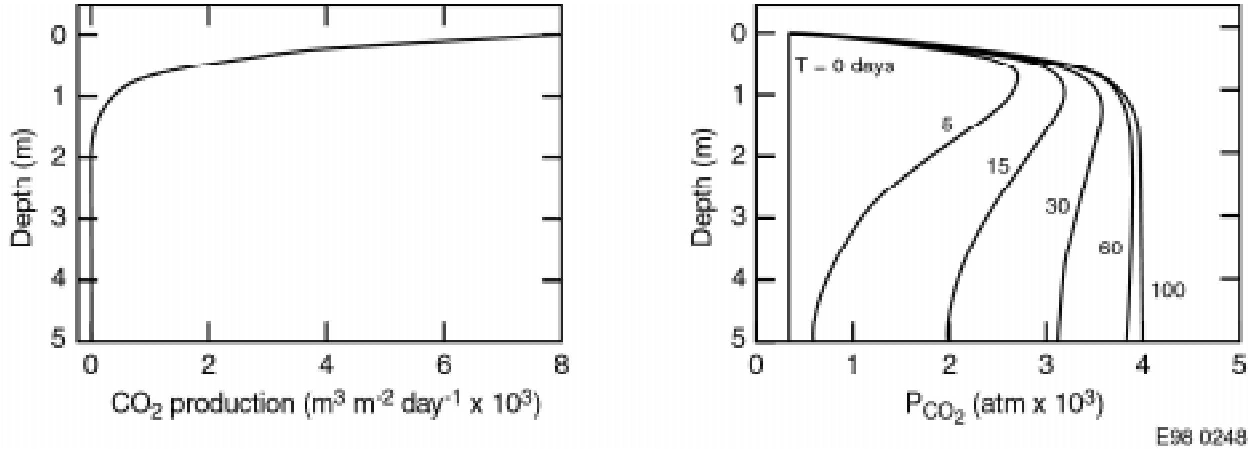

Figure 2. Vadose zone Carbon dioxide production as a function of depth (a) and the resulting carbon dioxide profiles as functions of time and depth.

maximum value at about 1-m depth. This maximum is the result of competing transport and production processes. Although the production rate is higher in the upper part of the profile (Figure 2a), diffusion of CO_2 to the surface and loss to the atmosphere prevent the build up of CO_2 in the vadose zone gas. At greater depths, the production rate is very low and the profile is dominated by the downward transport of CO_2 by gaseous diffusion. As time increase, the downward diffusion of CO_2 results in the development of a less pronounced maximum in the profile so that at later times (100 days) a steady state profile (for the upper five meters) is approached. This simplified example assumes constant production of CO_2 and ignores seasonal variations that would result from limited plant growth in the winter. In addition, no deep sources for CO_2 production such as the decomposition of buried organic wastes are considered. However, this example illustrates that under these simplified conditions, the CO_2 concentration (and hence pH) is both spatially and temporally variable in the vadose zone. This variability will occur even in the absence of advective transport of solutes. Because the adsorption of metal and radionuclides is highly pH dependent, the adsorption characteristics in the vadose zone will be highly variable. Typical performance and risk assessment modeling conducted for the vadose zone routinely assumes that the adsorption characteristics of the subsurface media are spatially and temporally constant, ignoring the variations resulting for vadose zone carbon cycle.

The Inverse Problem

The inverse problem is the problem of obtaining best estimates for the parameters in a distributed parameter system using experimental data. A distributed parameter system is a system that is represented by a mathematical model wherein specific processes are functions of some parameter that varies, in general, throughout the system. For example, the hydrogeologic flow equation for subsurface flow in porous soil depends on the soil permeability or transmissivity. The permeability may vary by several orders of magnitude in a subsurface region. This region may need to be modeled for the purpose of determining the potential for migration of contaminants through the vadose zone to an aquifer. The direction and rate of flow in the vadose zone depend critically on the distribution of soil permeability. The validity of any result produced by the mathematical model is critically dependent on a reasonable estimation of the permeability field.

The permeability is typically measured from core samples taken from wells drilled into the soil. Hydraulic head values are also measured in the wells. These data are only measured at a finite number of points in the domain of interest; the parameter values at intermediate locations must be estimated by some other means. The permeability can be estimated for the flow region given the known observations. A forward solution can then be performed to obtain predictions for the hydraulic head (the dependent variable of the flow equation). An iterative process is used to minimize the difference between the measured and predicted head values. The traditional method of adjusting parameter values is by trial and error. This is a very time consuming process and not the best way to proceed. This problem of estimating the soil parameters is what is referred to as the inverse problem and is actually a parameter estimation problem. A large number of techniques have been developed within the parameter estimation field and many of these have been applied to solve the inverse problem for hydrogeologic flow.

The Ill-Posedness Issue

The inverse problem is frequently ill-posed in a mathematical sense, Yeh (1986), Xiang, Sykes and Thomson (1992), Carrera and Neuman (1986a), Carrera (1987). Three types of ill-posedness that characterize the inverse problem are described in the literature:

- Nonidentifiability or nonsolvability—The model is not correctly defined; the model definition includes the describing equations, the boundary and initial conditions, any forcing functions and distributions of associated problem parameters.
- Nonuniqueness—There is not a one-to-one mapping between the parameter domain and the observation domain; there are multiple parameter fields that will produce the observed head field. If only point values are available in a distributed parameter system, the inverse problem is always nonunique (Chavent 1974).
- Instability—The solution does not depend continuously on the data; small variations in the data lead to large variations in the solution (Carrera 1987).

The root cause of the inverse problem being ill-posed seems to be insufficient data. This includes insufficient boundary and/or initial conditions, insufficient information about the parameter field, and insufficient knowledge about the describing equations. Hydraulic head data alone are usually insufficient to guarantee a stable and unique solution (Carrera and Neuman 1986a).

Approaches to the Inverse Problem

The articles authored by Yeh (1986) and Carrera (1987) provide extensive reviews of inverse problem issues and methods. They divide the approaches into two major categories — direct and indirect methods. The direct method was popular earlier, but has now fallen from favor to a large extent. The direct method involves a direct inversion of the model equations. This requires that the dependent variable field be known, which, of course, it is not. But it can be estimated by standard interpolation methods employing measurements of the dependent variable. The problem is then inverted directly to solve for the parameters. For the indirect method, it is not required to know the dependent variable field. An objective function can be defined wherein differences between measured and computed values are summed to obtain an overall measure of the ‘goodness’ of fit of the parameter field. The parameter field is adjusted based on one of several optimization algorithms available to reduce the objective function. This process is iterated until the objective function is minimized. The indirect approach requires the parameterization of the problem. The parameterization may be based on a geostatistical structure or some interpolating function to fully define the parameter field.

Parameterization

The mathematical model that represents flow in the porous medium is a differential equation that is based on the conservation of mass and Darcy’s law. Darcy’s law is an approximation of the true equations of fluid dynamics (representing the conservation of momentum) that makes the flow problem tractable. The differential flow equation requires the specification of the permeability at every point in the flow domain in order for the equation to be solvable; that is, the permeability must be specified at an infinite number of points. Because the standard approach for solving the describing model equations is to discretize the flow equation, the parameter field is reduced to being defined on a finite number of mesh nodes or cells. This reduction of the parameter dimension from infinite to finite is called parameterization.

An important issue associated with parameterization is that if one reduces the parameter dimension too much, large mass errors result; that is, the parameter field is probably inaccurately represented. However, if the parameter dimension is too large (insufficient data to support the parameter dimension), instability results. Thus, there is a trade-off between robustness and accuracy, Carrera and Neuman (1986), Yeh (1986). The optimal parameterization is dependent on the quantity and quality of available data, Yeh (1986). Yeh suggests that one can find the optimal parameterization by starting with a small parameter dimension and then increasing it while monitoring the mass errors versus the parameter uncertainty. Furthermore, Yeh and Yoon (1981) state that the number of parameters must be limited and substantially fewer than the numbers of observations (data values). This is called regularization ; it stabilizes the solution and allows for a unique inverse solution.

A number of methods have been developed to obtain parameterizations. The simplest is called zonation where the computational domain is simply divided into zones such that each one is assigned a specific parameter value. This method is robust and seems to work best when the parameter data are sparse, Keidser and Rosbjerg (1991). Another well known method for data interpolation is kriging. Kriging is a geostatistical method that involves assuming that a particular parameter distribution possesses some statistical structure. The structure relates to the variance of the distribution. The interpolation technique is a weighted average of nearby known values. The interpolation can be applied to points or to areas. Keidser and Rosbjerg (1991) compare four parameterization methods, three that involve kriging and the fourth pure zonation. In all cases, certain parameters are optimized to obtain best estimates for the transmissivity and other flow and transport parameters to solve the inverse problem. Each of the three methods that involve kriging imposes different structures to the final parameter fields. The first method employs the pilot point method wherein several points at which no observations exist are selected based on the sensitivity of the solution to their values. The parameter values at the pilot points are then optimized. The parameter field is then generated from the actual observations plus the optimized values of the pilot points as if they were also observations. New pilot points could be selected to add in a following iteration. The pilot point method is described by RamaRao et al. (1995).

The second kriging method is a hybrid kriging/zonation method. The field is divided into zones, similar to the zonation approach. Kriging is then applied to obtain the parameter field. Correction factors for each zone are then added to the kriged values to obtain the final parameter field. Optimizing the zonal correction factors constitutes the inverse problem for this method. The third kriging approach involves optimizing geostatistical parameters that relate to the variance of the interpolated values. Each of the above parameterization methods imposes a different set of constraints on the final parameter field while allowing different aspects of the field description to be optimized in order to fit the desired dependent variable data. For the study referenced above [Keidser and Rosbjerg (1991)], head and solute concentration values that are predicted by the flow and transport equations, respectively, are used to condition the parameter fields.

A significant study that compared seven inverse solution methodologies is reported by Zimmerman et al. (1998). The methods described in this study use a variety of parameterization techniques including Fast Fourier Transforms, stationary analytical forms, cokriging, an analytical form derived from fractals, pilot points, and common statistical methods (normal, non-Gaussian, etc.). Although no single method was judged to be superior, it was found that the nonlinear methods performed best for complex synthetic problems.

An important issue that is related to parameterization and also to the finite mesh deals with effective parameter values. When the parameter involved in the model equation such as permeability in Darcy's law varies significantly, especially within a given mesh cell, then an effective value for the parameter should be used for that cell. This effective parameter value is that value that will produce the same overall dependent variable difference across the cell as does the actual parameter distribution. For example, for a one-dimensional flow, if there are two different porous materials across which the fluid must flow, the effective value will be a function of the width of each material and its permeability value. If each material has the same width, the effective permeability will be much closer to the lower permeability value. Furthermore, if someone were to measure the permeability at a series of points along the flow path, none would equal the effective permeability value. This example indicates that conditioning the desired effective parameter values on essentially point measurements of the parameter is inappropriate. In fact, the effective parameter value is actually a function of the size of the finite cell. Hence, the finite mesh should be carefully fitted to the parameter field to minimize errors that might occur due to unnecessary smoothing.

Solving the Indirect Inverse Problem

The indirect method for solving the inverse problem actually involves performing a series of forward solutions, each time with an improved parameter field until the parameter field can no longer be improved or until improvements are small. The measure of the goodness of the parameter field is defined as the objective function. The objective function is typically a measure of the difference between predictions and measured data. The quantity, quality, and type of data critically influence the potential to obtain a suitable parameter field, that is, suitable for simulating such things as contaminant transport, predicting where the contaminant goes and how fast it moves. The method of adjusting the parameters directly affects how efficiently the optimum is found. Depending on the actual solution method chosen to obtain the inverse solution, certain measures of parameter field goodness can be obtained.

Objective Functions

Objective functions are defined by the user and depend on the amount and quality of measured data. Typically, the objective function is a sum of the differences between the measured and predicted values of the dependent field (head, concentration, etc.). The data may be weighted depending on its quality or the amount of information it contains. Anderman and Hill (1997) construct an objective function that is an additive combination of the sum of the squared, weighted, hydraulic head differences; the sum of the squared, weighted flow differences; the sum of the squared, weighted, prior-information differences; and the sum of the squared, weighted, advective-transport differences. Here, advective transport is the transport of a single particle in the flow domain. Another approach to the formation of an objective function or estimator is to use the sum of absolute values of differences, weighted by the inverse of the variance, Xiang et al. (1992). Xiang et al. claim that this estimator is more robust and can more effectively filter outliers in the data. When more than one data set is used for the inverse solution, each set should be assigned relative weights that account for the value of each set. Weiss and Smith (1998) present four methods of assigning weights to different data sets.

Data

Clearly, the need to solve the inverse problem is due to the lack of information regarding the parameter fields in question. How much data is needed to adequately overcome this situation? At this point, it only seems clear that more is better, better quality is better, and more different types of data are better. As quoted above, Chavent (1974) has stated that if only point values are available in a distributed parameter system, the inverse problem is always nonunique (ill-posed). Head data alone are inadequate to obtain a transmissivity field, Anderman et al. (1996), Carrera and Neuman (1986). Anderman et al. (1996) employ head data, flow data, and advective transport data. Keidser and Rosbjerg (1991) employ head and concentration data. They use the equation for the nonsteady transport of nonreactive solutes and compare predictions of concentration as a function of time at particular locations against the data. Weiss and Smith (1998) also employ head and tracer concentration data in their article. Furthermore Weiss and Smith show how to judge the relative usefulness of different data sets and how to determine what new data would be most useful to reduce the parameter field uncertainty. Clearly, different types of data, e.g., head data versus tracer concentration data, contain different kinds of information. Thus, it is important to employ data of different types to be able to extract the different information available in order to have any success at estimating the parameter field.

Solution Methods

A solution method is required to efficiently search for the optimal set of parameter values required for the parameterization. Such a method can also be described as an optimization algorithm. That is, given a set of initial guesses for the parameters that will define a particular parameter field, how can the optimal set be found? The optimal set is defined as the one that minimizes the objective function (as defined above). There are a number of well known algorithms that have been used with great success. Here we only mention the more popular ones. Many inverse methods employ a modified Gauss-Newton method, Anderman and Hill (1997). This method is the very well known Newton method with the Marquardt modification that is added to speed convergence for problems whose minimum lies at the bottom of a long narrow ‘canyon.’ Another class of methods is called conjugate gradient methods, Carrera and Neuman (1986b). This class of methods represents a modification to the method of steepest descent, employing the conjugate gradient of the steepest descent. Olsthoorn (1995) compares the four variations of conjugate gradient methods investigated by Carrera and Neuman (1986b) with the Levenberg-Marquardt scheme and finds that the latter is generally more effective. The Levenberg-Marquardt scheme is closely related to the modified Gauss-Newton scheme.

Statistical Measures of the Solution

By employing a statistical approach to the inverse problem, as opposed to the traditional trial-and-error method, particular measures of the ‘goodness’ of the solution can be performed. Weiss and Smith (1998) and Poeter and Hill (1997) describe how to obtain confidence limits on the parameter estimates. However, Zimmerman et al. (1998) indicate that confidence limits are not adequate to determine the ‘goodness’ of the solution. They recommend that multiple realizations of the forward problem be performed to give some measure of the uncertainty of the parameter estimates. The ensemble of realizations is apparently obtained from random variations of the best estimates of the parameter field, probably within some defined variance of the best values.

Summary

The goal of the three-year Reactive Transport in Variably Saturated Media Project is to develop a better understanding of the movement and transformation of reactive constituents in heterogeneous, variably saturated subsurface media (e.g., vadose zone) and parlay this better understanding into improved estimates of the fate and mobility of reactive constituents in the vadose zone. This is being accomplished by building upon existing INEEL expertise and through interactions with the university (and other) research communities. The project was initiated in February 1998 with the development of a detailed Science and Modeling Plan that provides detailed justification, scientific rationale, and technical approaches to be used in the project. An early draft of the Science and Modeling Plan was used as the basis for a workshop involving six university vadose zone researchers. The workshop was used to more fully develop and validate the scientific themes of the project. These theme have been translated into three specific tasks:

- Up-scaling of geochemical heterogeneity
- Propagation of geochemical environment in the vadose zone
- Integrated vadose zone characterization.

Each task has specific scientific goals and identified university collaborators.

Up-Scaling of Geochemical Heterogeneity. Biogeochemical processes occur at the pore-scale and involve interactions between advecting fluids, mineral surfaces, and microorganisms in a heterogeneous media. However, transport modeling is conducted at the scale of representative volumes. Often these representative volumes range from 10s to 100s of liters and require that the heterogeneity smaller than this be up-scaled and averaged. Although there has been much previous research on the up-scaling of physical heterogeneity, only limited research has been focused on the up-scaling of geochemical heterogeneity. To date, a theoretical up-scaling relationship has been developed for layering, a common subsurface heterogeneity. This relationship is based on the concept of effective reactive surface area, which is the surface area that is available to react with advecting solutes. A key feature of this scaling relationship is that the reactivity properties of the media will exhibit anisotropy with greater reactivity in the vertical direction and less reactivity in the horizontal direction. High-resolution numerical modeling of small-scale heterogeneity is being conducted to assess the implication of anisotropic effective reactive area to the transport of solutes using the computer code HYDROGEOCHEM. This task is being conducted in collaboration with Dr. George Yeh of Penn State University, the developer of HYDROGEOCHEM.

Propagation of Geochemical Environment in the Vadose Zone. Unlike groundwater systems, in the vadose zone, both advection of water and/or gaseous diffusion/advection can transport volatile reactive species. This task will focus on the role of gaseous transport of inorganic carbon in controlling the pH of advecting vadose zone waters. Inorganic carbon often controls pH in natural waters and can be transported by advective water movement [bicarbonate] or by gaseous diffusion or advection [carbon dioxide]. Ultimately, pH is one of the most important master variables in controlling reactive transport and other biogeochemical processes. Preliminary calculations of the effect of in situ CO_2 production on the distribution of CO_2 in the vadose zone have been made using the UNSATCHEM computer code. These results illustrate the CO_2 concentration (and hence pH) is spatially and temporally variable in the vadose zone even in the absence of advective transport. Furthermore, because the adsorption of metal and radionuclides is highly pH dependent, the adsorption characteristics in the vadose zone will be highly variable even in the absence of subsurface physical and chemical heterogeneity. Typical performance and risk assessment modeling conduct for the vadose zone routinely assumes that the adsorption characteristics of the subsurface media are spatially and temporally constant, ignoring the variations resulting from the vadose zone carbon cycle. Numerical simulations that include or exclude gaseous transport will be conducted and the effects on the reactive transport of a DOE-relevant actinide, uranium, will be assessed. Uranium will be used because it forms strong complexes with carbonate and occurs as either a cation or anion depending on the solution’s pH. This research is being conducted in collaboration with Dr. Donald Suarez of the U.S. Salinity Laboratory, the developer of the UNSATCHEM computer code.

Integrated Vadose Zone Characterization. A variety of characterization measurement techniques are available for the vadose zone. These measurements include point measurement (e.g., borehole vadose zone instruments), nonintrusive characterization (surface or cross-borehole geophysics), and processes measurements (e.g., reactive or conservative tracer breakthrough test). However, systematic approaches as to the distribution of measurement locations, number of measurements, and mixes of differing type of measurements that yield the maximum amount of information on the vadose zone are lacking. To date, a detailed review of inverse methods for hydrological model parameterization has been conducted. In addition, a review of available field sites and data has been conduced and included in the Science and Modeling Plan. Steps are underway to integrate inverse modeling approaches with field vadose zone measurements to define more realistic representations of vadose zone heterogeneity that include estimates of property uncertainties and allow the design of improved vadose zone characterization strategies. This task will include a significant field component, as detailed field measurements will be required. A collaborative relationship is being developed with Dr. Jim Yeh (no relation to George Yeh) of the University of Arizona. Dr. Yeh is considering a sabbatical leave at the INEEL starting in late FY 1999.

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TRANSPORT PHENOMENA IN GEOLOGIC POROUS MEDIA

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Scope and Objective

This program is part of the Core Capabilities/Technical Enhancement portion of the Validation, Verification, and Engineering Analysis Program. The Core Capabilities/Technical Enhancement activities include the following tasks: (1) Science and Technology Foundations, (2) Transport Aspects of Selected Mass Transport Agents, (3) Chemistry of Environmental Surfaces, (4) Materials Dynamics, (5) Characterization Science for Optimization of Waste Processing and Monitoring, and (6) Computational Physics, Chemistry, Geophysics, and Systems Analysis.

The Transport Phenomena in Porous Media Program is one part of Task 3 above and includes five subtasks:

1. Partitioning of Bacterial Populations between Mobile and Immobile Phases in Saturated Basalt. The objective of this subtask was to improve the ability to predict the location of microbial biomass and functions in saturated subsurface environments.

2. Computational Modeling of Microbial Processes and Chemical Transport. The objective of this subtask was to address the fundamental question of why lab studies sometimes fail to predict the behavior of a biodegraded plume in the field.

3. Utilization of Deep Tensiometers to Interrogate and Validate Numeric Models and Existing Field Data. The objective of this subtask was to collect, interpret, and integrate soil water potential data to improve the understanding of deep vadose zone transport based upon field measurements.

4. Steam Enhanced Extraction in Fractured Porous Media. The objective of this subtask was to conduct experiments that model steam condensation front position, velocity, and temperature profile during the steam-enhanced extraction process of removing liquid contaminants in fractured porous media.

5. Biologically Mediated Actinide Transport in the Subsurface: Saturated Zone Testing. The objective of this subtask is to better understand the coupling of microbial processes and surface geochemical reactions that effect the migration of actinides such as plutonium and uranium through unsaturated and saturated zones in the subsurface.

Technical Accomplishments

Background

TASK 1—Partitioning of Bacterial Populations between Mobile and Immobile Phases in Saturated Basalt.

The ability to predict the location of microbial biomass and functions in saturated subsurface environments should improve the effectiveness of in situ manipulations for targeted applications. Current understanding is evolving with respect to the geochemical and physical controls on general spatial location of microbes in saturated media. However, ambiguous findings have been reported regarding the relative partitioning of microbes and their functions between the mobile and immobile phases and the conditions that may predictably alter this distribution. This project is dedicated to the empirical determination of the segregation of bacterial populations and functions as mixed groundwater communities interact with geologic media so that *in situ* biotransformations can be effectively modeled and implemented. The work relies on laboratory core floods and packed columns constructed with Snake River Plain Aquifer (SRPA) basalt that are perfused with SRPA groundwater and destructively sampled so that both planktonic and sessile bacterial communities may be examined. Bacterial communities are assayed by: total cell counts, community-level physiological profiles (CLPP), heterotrophic plate counts and morphological diversity of colonies, relative abundance of phylogenetic groupings based on 16s rRNA directed oligonucleotide probes, and MPN determination of selected functional groups, e.g., methanotrophs. Initial studies are aimed to generally describe differences in microbial community structure and function based on the microbial ecology of the system while subsequent studies focus on populations responsible for desired processes, e.g., co-metabolic degradation of TCE by methanotrophs. The effect of hydrogeology of the system as represented by fracture flow and porous flow on community partitioning is being investigated in replicated experiments with core floods constructed of basalt core with natural fractures and packed columns of the same material, crushed. Incorporation of nutrients, contaminants and manipulations to enhance degradation in the model system of these contaminants represent stepwise progressions in the complexity of the research. Direct examination of community response to hydraulic conductivity on fracture surfaces with a confocal scanning laser microscope is being conducted in collaboration with Dr. Al Cunningham, Montana State University. Field work will occur in a fractured basalt system by pumping water from a fractured zone through a similar “column” at the surface followed by laboratory examination of the communities. For porous media, field investigations of core and groundwater communities of samples retrieved from a shallow, sandy aquifer at the National Center for Integrated Bioremediation Research and Development (NCIBRD) at Wurtsmith Air Force Base, Michigan, are in progress. This location is the site of an intentional release of labeled hydrocarbons into the aquifer. The ultimate goal of the basic research embodied in field and laboratory investigations is to develop the most economical methods to characterize microbial heterogeneity at a particular site so that in situ manipulations may be efficiently conducted with results predictable by the appropriate numerical model.

TASK 2—Computational Modeling of Microbial Processes and Chemical Transport. The objective of this subtask was to address the fundamental question of why lab studies sometimes fail to predict the behavior of a biodegraded plume in the field.

This task addresses the fundamental question of why lab studies fail to predict (in many cases) the behavior of a biodegraded plume in the field. One suggestion that has emerged from these studies is that laboratory studies of degradation rates of contaminant by microorganisms often take place in an essentially homogeneous environment; on the other hand, the "field" offers a heterogeneous environment. In particular, the inhomogeneous distribution of the microorganisms may in the subsurface may render even a nominally homogeneous environment (e.g., sand) heterogeneous. This is the result of theoretical studies. In this study we explored the sensitivity of this conclusion to variations in the trapping rates.

TASK 3—Utilization of Deep Tensiometers to Interrogate and Validate Numeric Models and Existing Field Data.

The scope of the deep tensiometers task is to collect, interpret, and integrate soil water potential (SWP) data to improve the understanding of deep vadose zone transport based upon field measurements. This task uses the deep (advanced) tensiometer, invented at the INEEL, to collect the first direct measurements of soil water potential at depths below a few meters using standard borehole installation techniques. The specific objectives of this project include: (a) maintain and expand existing monitoring sites in arid and humid environments to produce data sets showing temporal variations of SWP in deep vadose zones for fractured rock and sedimentary materials, (b) initial evaluation of spatial variation of SWP in deep vadose zones for fractured rock and sedimentary materials, (c) preparation of a manuscript and dissemination of the results of field measurements from deep vadose zones, including presenting data at conferences to assist in forming collaborative investigations to evaluate deep vadose zone processes, and (d) conceptualize a design for an integrated instrument array for monitoring subsurface biological processes.

TASK 4—Steam Enhanced Extraction in Fractured Porous Media.

Experiments were successfully conducted that model steam condensation front position, velocity, and temperature profile during the steam-enhanced extraction process of removing liquid contaminants in fractured porous media. The SEE process consists of steam injection into porous media that is unsaturated, or partially, or completely saturated with contaminated water. Steam condensate, which contains the contaminant, is then pumped out at another location. The process is being considered for implementation for removal of contaminants in the vesicular basalt flows that lie above the Snake River aquifer at the INEEL.

TASK 5**—**Biologically Mediated Actinide Transport in the Subsurface: Saturated Zone Testing.

The primary objective of the proposed research is to better understand the coupling of microbial processes and surface geochemical reactions that effect the migration of actinides such as plutonium and uranium through unsaturated and saturated zones in the subsurface. Two research thrusts are proposed to fulfill this objective. The first thrust is to derive relationships between sediment physical characteristics, moisture content, and biogeochemical reactivity. Laboratory research to understand the effect of anaerobic microbes, as well as the effect of oxidative conditions postremediation, on the mobility of uranium in saturated zones, which is the second thrust of the project, was performed. The conceptual model for this task was developed by Integrated Earth Sciences personnel, while laboratory research to understand the effect of anaerobic microbes, as well as the effect of oxidative conditions postremediation, on the mobility of uranium in saturated zones was performed within the Biotechnologies Department.

Moisture Content and Effective Reactive Surface Area

A key uninvestigated aspect of the vadose zone biogeochemistry of contaminants is the coupling of microbial processes and surface reactions to the distribution of water within unsaturated subsurface media. Previous research conducted at the INEEL has focused on the biogeochemistry of uranium-citrate mixtures in fully saturated heterogeneous soils and sediments (Smith et al. 1996 a,b, Tompson et al. 1996). Theoretical considerations suggest that chemical reactivity ($K_{d,m}$) and permeability (k) are inversely related (Smith et al. 1996a).

$$K_{d,m} = \frac{K_{d,s}}{\rho} \frac{\phi}{1-\phi} \sqrt{\frac{\phi}{2\tau k}} \qquad (1)$$

Where $K_{d,m}$, $K_{d,a}$, ρ, ϕ, and τ are the mass-based distribution coefficient, the surface area-based distribution coefficient, grain density, porosity, and tortuosity, respectively. The correlation arises because $K_{d,m}$ and k are functions of the surface area of the porous media. This relationship is consistent with observed biogeochemical reactivity, surface area, permeability, and porosity data for monomineralic sediments (i.e., quartz sand) and hydrous oxide (goethite)-coated sediments. In the case of coated sediments, explicit consideration of the nature (porous vs. nonporous) and abundance (extractable iron content) of the coatings is required to describe the relationship between reactivity and permeability. The relationship described by equation (1) indicates that zones of high flow and low reactivity will dominate the movement of water and nonreactive (with respect to the geologic media) electron acceptors such as oxygen or nitrate. Conversely, reactive (with respect to the geologic media) nutrients and contaminants such as phosphate and actinides will be sequestered in zones of low flow and high reactivity. This physical framework will result in biologically active zones distributed in the subsurface at the boundary between these flow zones.

In the unsaturated vadose zone, the relationships between physical and geochemical heterogeneity and biogeochemical reactivity will be much more complex and will vary as a function of moisture content. Near conditions of saturation, the majority of flow will occur in the largest pores. Because of capillary force, these large pores will be dry and inhospitable to subsurface microorganisms at conditions of lower moisture content. Although the smallest pores will remain saturated under all but the most extreme drying, bacteria will be excluded from these pores because of their size. Additionally, the amount of reactive surface area in the geologic media is inversely related to the pore size. For example, unpublished surface area and pore size distribution measurements for INEEL basalts indicate that greater than 95% of the total surface area of basalt occurs in pores of less than 1 μm. Coupling variable moisture content, reactive surface area, pore size distributions, and bacteria with finite size will result in a complex relationship between sediment structure, moisture content, and biogeochemical activity.

Microbially Mediated Uranium Transport in Saturated Aquifer Material

In saturated subsurface environments throughout the DOE complex, chlorinated hydrocarbons and actinides are two of the most common contaminants. While a large amount of fundamental and applied knowledge has been gained regarding reductive dechlorination of chlorinated organic contaminants, the effect of these changes to the subsurface chemistry on mobility of actinides that have complexed to mineral surfaces has received limited attention. Microorganisms may effect the mobility of the actinide directly by changing the speciation, or indirectly by effecting the mineral matrix to which the metal has complexed. The first objective of the proposed research is to perform bench scale experiments to gain a basic scientific understanding of how reducing conditions caused by indigenous microbial populations stimulated to biotransform chlorinated contaminants effect mobilization of actinides that have become chemically sorbed to basalt. A second objective of this portion of the research will be to determine the effect of oxidative conditions established after accelerated bioremediation has been performed and the saturated zone is returned to oxidative conditions on actinide mobility. Knowledge gained from the project will be directly applicable to the contaminant plume at Test Area North and the ongoing record of decision (ROD) in place to remediate the organic fraction of the plume.

The bench-scale laboratory research will attempt to address a largely ignored issue associated with in situ remediation—the potential enhancement of mobility of co-disposed radionuclides resulting from remediation of organic groundwater contaminants. When microbial growth conditions are established in the subsurface for chlorinated solvent biotransformation, changes in chemistry will effect the fate of the uranium that has become chemically complexed to the geologic media. Anaerobic microorganisms require certain environmental factors to be favorable to maintain their baseline physiology as well as dechlorination activity. One important factor is the redox potential (Eh) of the growth medium. A change in Eh facilitated by microorganisms has a strong possibility of affecting other chemistries in the area of changed Eh (i. e., metal mobility and speciation). The hypothesized mechanism of uranium release from the U-mineral oxide complex is similar for both methanogenic and sulfate-reducing conditions. In this mechanism uranyl ions sorb to mineral oxides such as iron oxide, ferric oxyhydroxides or manganese oxides. For the purpose of the research, iron oxide minerals will be of primary interest. Once accelerated bioremediation is initiated, the required redox for microbial growth and supplementary electron transfer occurring in the system leads to the reduction and loss of the iron oxide and uranyl ions. The uranyl ions will complex with carbonate forming dioxouranium (VI) carbonate complexes. The iron is lost as ferrous iron, which may form carbonate complexes. Under methanogenic conditions, the uranium carbonate will stay in solution depending on the microbial activity occurring or will be precipitated as solid uranous oxide. Uranium solubility will be effected under conditions of sulfate reduction due to the formation of metal sulfides, specifically iron sulfide. Two potential effects of the iron sulfide would be abiotic reduction of the U(VI) and reprecipitation onto the mineral matrix, or adsorption to iron sulfide particles followed by precipitation. The effect of oxidative conditions established after accelerated anaerobic remediation has been completed and the groundwater returns to oxygenated conditions on uranium mobility will also be determined.

The thrust of this phase of the project will be to study the affect of changes in the oxidation-reduction potential of the groundwater on the mobility of geologically complexed actinides in saturated subsurface media, specifically basalt. The specific goals of the proposed research are to:

- Demonstrate a link between anaerobic bioremediation of chlorinated contaminants and the mobilization/immobilization of uranium from basalt and iron oxide minerals
- Understand the mechanisms responsible for the release of uranium from specific mineral components (e.g., mineral oxide compounds) during anaerobic bioremediation
- Understand and develop adsorption/desorption kinetics for uranium mobilized from basalt and iron oxides under sulfate-reducing conditions
- Understand and develop adsorption/desorption kinetics for uranium mobilized from basalt and iron oxides under methanogenic conditions
- Understand the mechanisms for the release of uranium from mineral oxide compounds during reestablishment of oxidative conditions in groundwater.

The effect of remediating trichloroethylene using sulfate-reducing and methanogenic conditions on actinide mobility will be determined. Previous research at the INEEL has shown that sulfate-reducing and methanogenic enrichments are able to transfer electrons to organometallic compounds effecting the valence state of transition metal involved. The initial research task, which spans the first year, will be to determine the interaction of redox conditions on uranium using simulated materials to mimic the mineral matrices found on the surface of basalt. Batch testing will be performed during this phase of research. When culture conditions are established in the subsurface, changes in chemistry will effect the fate of uranium that has become specifically sorbed to basalt. After remediation of the plume is complete the aquifer in the area will naturally return to oxidative conditions. The effect of the positive oxidation reduction potential on the chemically sorbed uranium will be determined.

The second thrust of this phase of the research, which is scheduled for FY 99, will be to perform column experiments using uranium-contaminated basalt. This phase of the research is scheduled for the second year of the project. Near the end of the batch testing, using simulated minerals, samples of basalt will be crushed and contaminated with uranium. The second year of research will involve studying the effect of sulfate-reducing conditions on the solubilization of uranium from basalt in continuous flow columns. Columns will be set up and packed with crushed uncontaminated basalt. The columns will be flooded with a uranium solution, allowing for sorption of the uranium to the mineral surface. Mixed microbial consortia enriched from basalt and/or groundwater will be used for the experiments. To better simulate field conditions, pure cultures will not be used during testing. Groundwater and basalt will be enriched for sulfate-reducing and methanogenic bacteria, by adding sulfate to or deleting sulfate from the groundwater. The sulfate concentration of the groundwater will be determined prior to testing. Sulfate-reducing conditions will be established by adding sulfate to the groundwater being pumped into the column. Methanogenic conditions will be established using sulfate-free groundwater. Lactate will be used as the carbon and electron source depending on the enrichment method used. Continuous flow experiments will be set up and run for a period to allow for simulation of field conditions. The short timeframe of the experiment is thought to be adequate due to the nature of accelerated bioremediation. A range of redox potentials will be noted over the length of the column. The inlet of the column will be closer to aerobic conditions where the redox potential will be high with low concentrations of oxygen present. As the solution passes through the reactor simulating a remediation operation the redox will decrease to levels optimum for SRBs or methanogens depending on enrichment. Exposure of these low redox chemistries to the contaminated mineral matrices will allow potential substitution at the mineral interface.

The bioreactor influent and effluent will be monitored for TCE and associated transformation products, Eh, pH, sulfide, uranium as well as metals associated with the mineral matrix. Once adequate data has been gathered regarding desorption of uranium from the basalt under conditions conducive to accelerated anaerobic bioremediation, oxygen will be added to the bioreactor and eluted through the test column to determine the effect of oxidative conditions on uranium mobility in a continuous flow system. The final year of research will encompass studies to ascertain the effect of methanogenic conditions and subsequent oxidative conditions on the mobilization of uranium from basalt.

FY 1998 Accomplishments

TASK 1—Partitioning of Bacterial Populations between Mobile and Immobile Phases in Saturated Basalt.

Progress will first be reported for these three related subtasks:

- Subtask for complete lab analyses on Replicated Hydrogeology (RH) experiment performed in FY-97)
- Perform basalt surface area analysis for RH cores subtask
- Analyze, reduce, and interpret RH experimental data subtask.

Experimental RH data was reduced, analyzed, and presented in a platform paper at The Eighth International Symposium on Microbial Ecology, Halifax, Canada, August 1998. A manuscript for refereed journal submission is in preparation. Surface area determinations suggest a factor of two for linear tortuosity of a single linear surface dimension with a small degree of detectable directionality to this constant (i.e., vertical vs. horizontal aspect of basalt flow). This method is highly laborious; results compared with automated laser technique confirm necessity of laborious direct observations. Critical RH experimental results and conclusions follow:

Total cell counts from packed columns (porous flow) solid and liquid phases are expressed in several ways (see Figure 1) with error bars representing the standard deviation of five independent replicates. Conventional expression is per ml for water and per g for solids. To more accurately compare these, the data was normalized by cc of in situ media taking into account the in situ porosity and the rock was also expressed by volume of rock (pure) taking into account the specific gravity of the basalt. The normalizing of the data even widens the gap between overall cells attached and unattached in the crushed basalt columns so that less than 1% are seen freely floating—this result is consistent with most literature findings.

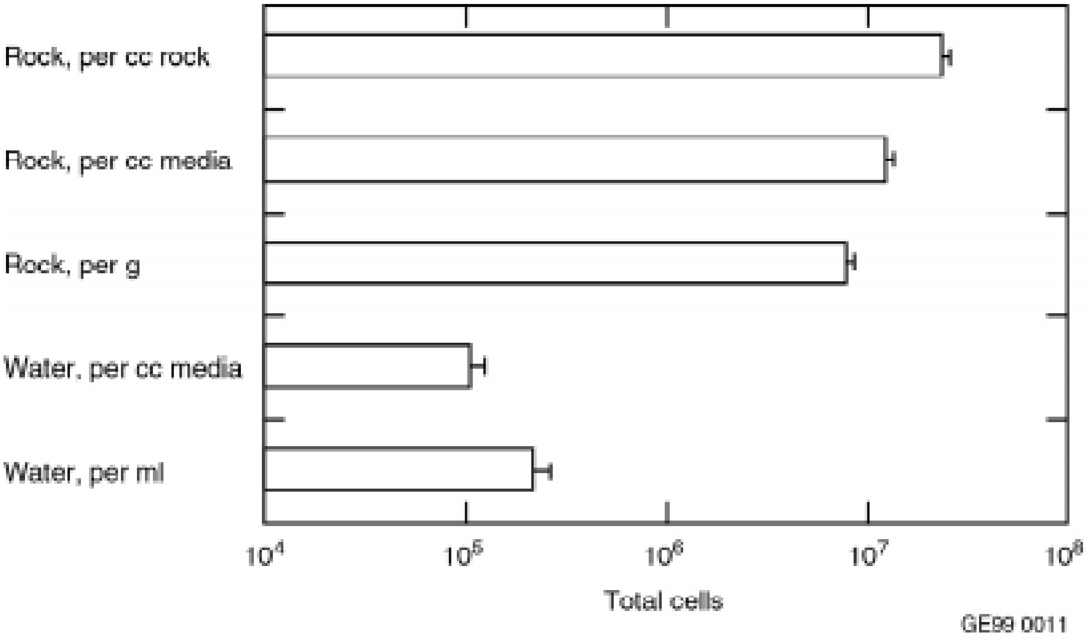

Figure 1. Total cell counts from packed columns.

Cells on fractures are not normally expressed separately in field sample results. Their contribution is usually included in a bulk volume value based on grams. In our study of fractured columns (see Figure 2), the face was scraped separately of the bulk phase and quantified; however, the number per ml of extract is not useful because it is based on an arbitrary volume of extract. Normalization per cc of fracture volume again results in a predominance of water vs. rock; about 10% of the total cells were found to be planktonic. But, using fracture volume may be misleading; the width of the fracture with affect this ratio, regardless of other factors. No unequivocal comparison appears possible.

To compare the attached cells in the two treatments, the total cells were reported on a surface area basis. For the fractured column, the number of cells were expressed by square centimeter of surface area derived from the geometric dimensions of the two fracture phases summed and multiplied by a tortuosity factor based on micro-morphometric examination of the fracture surface. For the packed columns, the analogous expression (with correction results in the greater than 10^5 value at the bottom of the chart. The results are shown in Figure 3. If all surface areas [internal by BET (data via Bob Smith) and external] are combined, then this value decreases by three orders of magnitude. But, much of the internal area is connected by pore throats less than 1 micron in diameter and therefore inaccessible to microorganisms; accounting for the accessible internal surface area (mercury porosimetry data via Bob Smith), the value for the packed column is mid-10^4—just slightly less than the fracture value and not significantly different ($P>0.05$; 1-way ANOVA). This overall result is significant because it disproves one of the original hypotheses—that partitioning of biomass would be affected by the hydrogeology (porous vs. fracture flow) that was based on several observations on field samples from chalcopyrite, basalt, and literature findings. The result also leads to some new interesting conclusions—namely, that field samples may underestimate the importance of attached organisms due to (1) inability to discriminately sample fractures; and, (2) propensity to contaminate fractures during sampling and sample processing. Further complicating interpretation of field data is the influence of hydraulic conductivity. The velocity of fluid flow may affect the partitioning of organisms (hypothesized). In most fracture-flow environments, K is much higher than in porous environments. The covariate nature of K with the type of flow may explain some of the difference in field and laboratory results.

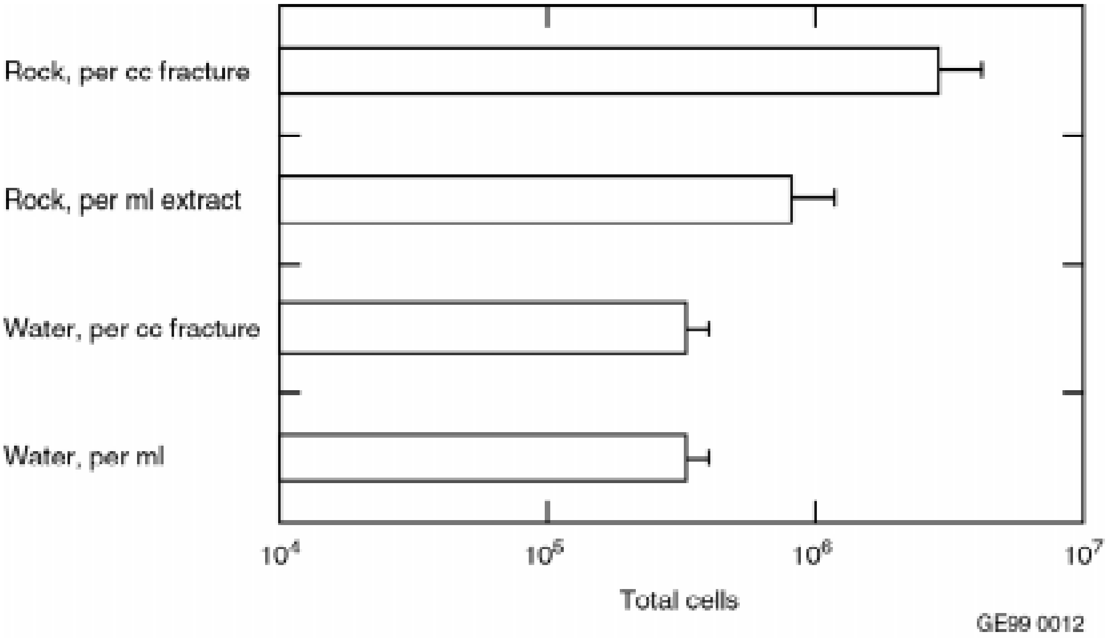

Figure 2. Total cell counts from fracture columns.

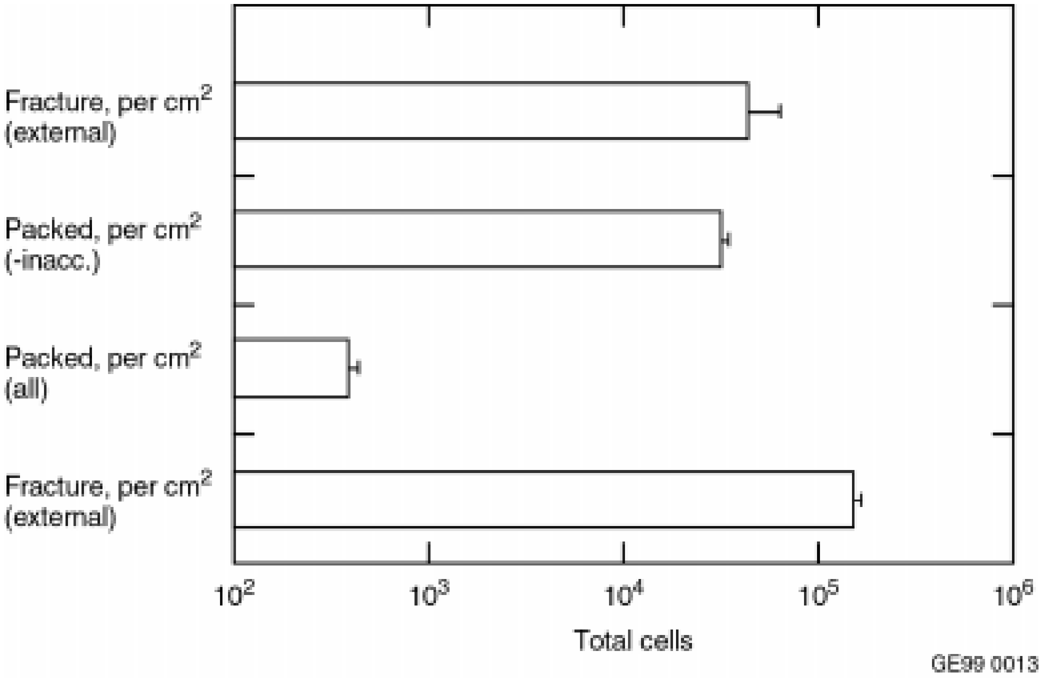

Figure 3. Total cells on solids by surface area.

Summary of other RH experimental results

- Phenol-oxidizers somewhat enriched on fractures (could be result of natural precipitates on fractures, not packed material, that enhance sorption of these physiological types).

Fatty acid methyl ester (FAME) analysis of isolates corroborated colony morphology

- Both g+ and g- organisms present, e.g., Arthrobacter, Bacillus sp., Pseudomonas sp.
- Little segregation in taxonomic identities
- No methanotrophs in water or rock
- CFU's parallel total cell counts; high apparent percent culturability
- CLPP showed that attached and unattached communities had significantly different carbon-source utilization patterns in both types of columns
- Number of carbon sources used was not significantly different by either treatment (type of column) or location (attached vs. unattached).
- The diversity of colony morphotypes was not significantly different by either treatment (type of column) or location (attached vs. unattached).

Conclusions from RH study

Units are critical for comparison of water and core microbiota as well as solids from different hydrological regimes. Using an enrichment factor for similar systems may prove most useful. In comparing attached and unattached organisms in saturated subsurface materials, the usual problems facing microbial ecologists are exaggerated because of the different matrices and extreme caution should be used in interpreting the results. Typical problems encountered that affect validity of conclusions from experimental data include: culturability; extraction efficiency; masking of direct observation; detection limits of various methods; and determining the exact measure that a particular approach actually returns. Two types of approaches seem most promising—directly labeling whole cells with phylogenetic probes (e.g., FISH) and using ratios of mass-dependent measures or concentration on mass-independent measures (although extraction efficiency still affects the latter). We have spent and will continue to spend time on optimizing FISH approaches for these types of samples. To date, the successful application of FISH is mostly confined to samples with lots of biomass or very active cells. This work is worth pursuing as the value of the measure would be great in objectively distinguishing between attached and unattached communities. With respect to field samples, there is great difficulty in obtaining uncompromised samples from fractures (crystalline rock) and deeper, unconsolidated sediments (porous media). Further, the co-variance of K with the hydrogeology of these systems needs to be accounted to interpret field results

Extraction experiment subtask:

A laboratory experiment was conducted to determine the most efficient extraction methods to remove bacteria from basalt by Sandy Fox (LMITCO). Critical results and conclusion from this study follow:

A 3X2 ANOVA experiment testing the effect of extraction solution and separation method on obtaining total cells and community aggregate catabolism from basalt was conducted. Results (see Figure 4) did not show a main effect on total cells extracted by either solution ($P=0.127$) or separation method ($P=0.704$) any treatment although trends in the results indicated that sodium pyrophosphate generally had higher cell yields (data not shown). The results of the community carbon source utilization (total of 95 tested) indicate significant enhancement of cell extraction from basalt ($P<0.05$) by sodium pyrophosphate over PBS and water. Within the pyrophosphate extraction treatment, the effect of the separation treatment was in the following order: density>floc>slow. There was no significant difference between the density and floc treatments (due to variation in floc reps) and there was a significantly greater cell carbon source response in extracts separated by the density-gradient centrifugation method vs. slow centrifugation. We usually use the "Floc" method and will continue to do so as the density-gradient method is considerably more labor intensive and did not provide clear improvement in extraction efficiency.

Subtasks on effects of nutrient enrichment and contaminant presence on partitioning:

These tasks are currently ongoing. Highlights include an interaction with Montana State University (Dr. Al Cunningham) on implications of hydraulic conductivity on bacterial partitioning. Results of this task are expected to allow some of the surprising results from the RH study to be fully developed for peer-review publications, e.g., Repeat fracture corefloods and investigate interior of basalt matrix for microorganisms.

Direct observations of organisms on basalt subtask**:**

As an outgrowth of Al Cunningham's visit this year, we have been exploring some areas of mutual interest. At present we have agreed to spend incremental effort pursuing the following: Two fracture halves from the INEEL studies will be digitally scanned in 3-D at the 50 micron-level of resolution. From this data, Ernest Wisser (Ph.D. candidate) will reconstruct the fracture and resulting aperture. Then, by using numerical simulation, different bulk flow rates will be simulated and the local flow rate at given points along the fracture aperture will be calculated. From this flow map, a map of shear force is developed. The shear force map can then be compared to the map of stained biomass (by confocal) attached to the surface at a given bulk flow (K). The importance of this work is the effect of K on the

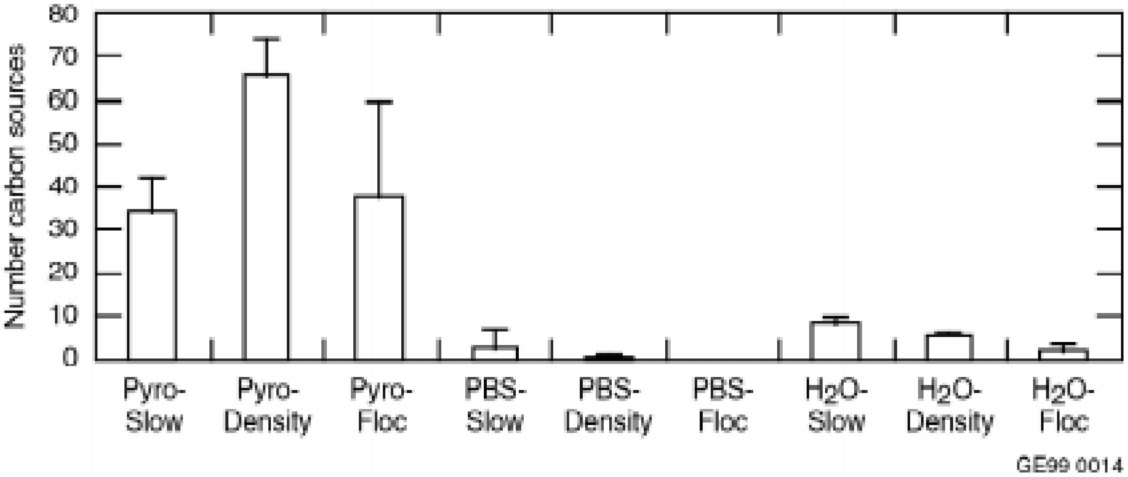

Figure 4. Sole carbon sources used by extractant.

attachment and physiology of attached bacteria. Is the real effect due to physical shear force on the cells or to bioavailability through nutrient transport mechanism (e.g., interaction of advection and diffusion)? Other methods of preparing biofilm for confocal microscopy are being investigated through literature review and conversations with professional conference presenters.

This subtask could benefit from increased collaboration with personnel working on Bill Bauer's LRP project—as time for the appropriate individuals is available.

NCIBRD collaboration subtask:

Collaboration with Dr. Michael Barcelona at NCIBRD continues. The objective of our work is to examine dynamics of attached and unattached aquifer communities [field samples] during contamination and subsequent remediation at MIRTL2 (intentional introduction of contaminants to aquifer). Proposal originated by Dr. Michael Barcelona (director, NCIBRD) describing MIRTL2 is available for inspection. The first samples were just received after the site visit for reconnaissance and introduction to field personnel in May 1998. Larger bolus of samples is expected in early fall. Additional site visit to assist in field sampling is projected.

Subtask for support of theoretical scenarios for computational modeling of contaminant fate and transport (Randall Laviolette):

Determined the following potential alterations to computational fate and transport model to reflect dynamic partitioning of microbes in saturated porous media to be worthy of investigation (from INEEL experimental study results and literature findings):

- Influence of trap distribution, e.g., log normal with respect to some injection site or other datum
- Influence of trap size; log normal frequency distribution with respect to a given average biomass (but still randomly distributed occurrence of traps)
- Combinations of a) and b)
- Even distribution, but randomly distributed magnitude of traps
- Inclusion of homogeneously distributed traps as % (changing) of total traps. Different degradation potentials (or distribution of potentials) assigned to each fraction.

Notes: Scale of heterogeneity to be considered in the model is the main issue for relating computational modeling and laboratory physical models, e.g., microbial measurements on linear 10^{-2} cm scale versus cm^3 bulk measures. These two types of measures are much different; computational model developed by Randall Laviolette (LMITCO) is considering the former while the partitioning experiments involve the latter. Literature vaguely suggests that cells in the environment exist as microcolonies and single cells. Considering the scale of measures in the experimental core floods and the focus on nonkinetic (e.g., not fraction collection and analysis of single pop.), little room exists for direct applications of computation models to physical models. Results of physical models (and effects of new variables) might be best estimated by simple multiple regression techniques.

Subtask for supporting the development of in situ sensors for activity of vadose zone microorganisms (J. Hubbell and Buck Sisson, LMITCO):

Several discussion sessions were held and a couple feasible options for development of downhole biosensors for the vadose zone were chosen for further study. Additional information is available in the Task 3 section of this report.

TASK 2—Computational Modeling of Microbial Processes and Chemical Transport. The objective of this subtask was to address the fundamental question of why lab studies sometimes fail to predict the behavior of a biodegraded plume in the field.

The pace of this task was substantially impacted due to the unexpected departure of an Associated Western Universities Research Fellow from the program. In spite of this set back, progress was made. The effect of log-normal distributions of trapping rates on the (uniformly) randomly placed trapping sites was investigated. Previously, trapping rates were taken to be identical on traps, however, log-normal distribution has been found experimentally in soil samples. Replacing the constant trap rate with the log-normal distribution amplifies the anomalies first found for the constant trap rate, by up to an order of magnitude. This discovery will be documented in a separate manuscript. Additionally, a new Windows interface was written for the transport code that allows real-time animation of the evolution of the plume.

Presentations:

- Presented the Biological Sciences Department Seminar at Idaho State University, October 2, 1997, on the subject of this research.
- Presented a brief summary of this research at the 78th Statistical Mechanics Meeting at Rutgers University, December 14, 1997.
- Submitted a manuscript to Geophysical Research Letters, May 20, 1998, entitled "Anomalous degradation kinetics in intrinsic biodegradation schemes," R. A. LaViolette, M.E. Watwood, T.R. Ginn, and D.L. Stoner. (received a recommendation to resubmit to Journal of Contaminant Hydrology).

TASK 3—Utilization of Deep Tensiometers to Interrogate and Validate Numeric Models and Existing Field Data.

The subsurface movement of moisture is the primary means by which contaminants are transported through the vadose zone and to the aquifer. Field data, obtained by instrumentation, are required to monitor these migration phenomena and provide data for model calibration. These data are needed to monitor and verify landfill and hazardous waste site conditions and evaluate contaminant plume movement. Deep tensiometers are one of the vadose zone instruments used to determine the potential for moisture movement, to determine the initial moisture conditions, for obtaining characterization data, for input to risk assessment modeling for determination of remediation action plans, and as a postclosure monitoring system to ensure the remedial action is effective. The deep tensiometer provides data not previously attainable that is critical for understanding transport through deep vadose zones. The tasks of this project are discussed individually in the following sections.

Maintain and expand existing monitoring sites in arid and humid environments to produce data sets showing temporal variations of soil water potential in deep vadose zones for fractured rock and sedimentary materials:

Instrumented wells at the IRC (W03, W04 and W05), Oak Ridge (Bear Creek site), RWMC (76-5, 77-2, and 78-1), Site 14 (south of TAN) and ICPP were maintained to collect SWPs in different geologic media and climatic conditions. They represent semiarid and humid sites in geologically diverse materials including sediments (gravel, sands, clay, and silts) and porous rock (basalt). Data was collected on an hourly basis and down loaded on a monthly or semimonthly basis. A large data base has been compiled for these sites and is available for further evaluation and analysis. Deep tensiometers were operated for time-periods of nine months to three years at depths of 3 to over 30 meters below land surface. Water potential measurements from wells at the semiarid site are all within the tensiometeric range of +100 to –220 cm. Tensiometers located in sedimentary materials had water potential in the range of 0–220 cm. Instruments within 3 m of land surface show the influence of ET with higher SWP in the spring and lowest SWP in the fall and winter. Instruments at deeper depths at semiarid sites show relatively stable measurements with no discernable changes in SWP related to infiltration of precipitation except at one site where an instrument was located within sediments immediately above fractured rock. The fracture rock sites have water potentials in the range of 50 to -220 cm. All of the tensiometers in fractured rock are located at depths exceeding 3 m.

The tensiometer data suggests that there may be a relationship between the textural and infiltration characteristics that limits the effective range of SWP measurements (Sisson and Hubbell, 1998). Temporal variations in SWP indicate significant infiltration that can be seen below 2 m in the spring at selected sites. The shallowest instruments at 2–3 meters indicate the greatest influence of infiltration and evapotranspiration, while greater depths show no discernable fluctuations (Hubbell and Sisson, 1998). Hydraulic barriers may cause formation of perched water for short time periods (days/weeks). The relatively uniform water potentials obtained with depth indicated the hydraulic gradient to be downward and near unity at both wells. Thus water movement was downward at a rate near the hydraulic conductivity. Tensiometers in one well showed episodic moisture movement to depths of 15.5 m in a few days after snow melt events.

The humid site has SWP measurements in the range of 0 to -350 cm. The shallowest tensiometer at 0.5 and 3.6 ft have the widest variation in measurements but all depths react to infiltration events. Several tensiometers are located beneath the water table and provide evidence of rapid recharge to the aquifer from lateral flow.

Deep tensiometer field data were used to determine that barometric pressure fluctuations influence measurements from tensiometers. This effect is caused by a pressure imbalance between the reference pressure (barometric pressure) and pressure in the soil gas at the measurement depth. The magnitude of the effect appears to be related to several interrelated properties of the geologic media including: the texture, air permeability and moisture content. Tensiometers located in higher permeability (air) materials (gravel and sand) appear to be least impacted. The barometric pressure fluctuation effect appears to have a seasonal component that is greatest in the winter and early spring. Laboratory and field tests were conducted to ascertain if isobaric (equal pressure) tensiometers are feasible and practicable (a tensiometer that automatically removes “noise” from barometric pressure changes). These tests suggest that a portion of the noise can be removed. A patent application was prepared and submitted for the isobaric technique (groundwater and vadose zone instruments) to the United States Patent and Trademark Office.

Initial evaluation of spatial variation of soil water potential in deep vadose zones for fractured rock and sedimentary materials.

A new well was instrumented with deep tensiometers at the IRC site to provide additional data for evaluation of spatial variability. Over a distance of tens of meters laterally, the SWP has minor, but discernable, differences controlled in part by differences in lithology and spatial distribution of infiltration. The water potential distribution appears to be primarily influenced by lithology, i.e., variations in permeability with depth. In the distance of tens of km laterally, the water potential has greater variation than from the smaller scale but within the range of 0–300 cm. The twin well site show measurements over an 8 m distance has SWP variations of about 50 cm between the same depths in the wells. Perched water formed at the same depth in both wells. Measurement of SWP at sites can be used to generalize the overall range of measurements in fine sediments but specific measurements are required at sites with the potential for preferential flow.

Preparation of a manuscript and dissemination of the results of field measurements from deep vadose zones, including presenting data at conferences to assist in forming collaborative investigations to evaluate deep vadose zone processes:

A description of the design, construction, use, and data from deep tensiometers was presented at the poster presentation for the international conference on “Characterization and measurement of hydraulic properties of unsaturated porous media,” held in Riverside, California. This conference was hosted by the Nuclear Regulatory Commission, the U.S. Geological Survey and USDA-ARA Soil Salinity Laboratory and was attended by over 200 scientists from about 25 countries. Information on the advanced (deep) and portable tensiometer were presented and discussed in the presentation on advances in vadose zone monitoring technologies. The paper entitled “Water Potential to Depths of 30 Meters in Fractured Basalt and Sedimentary Interbeds” was prepared and submitted for inclusion in the book to be published on this conference.

Field data from deep tensiometers was presented at the 1997 Joint American Geophysical Union Chapman/Soil Science Society of America Outreach Conference on “ Application of GIS, Remote Sensing, Geostatistics, and solute transport modeling to assessment of nonpoint source pollutants in the Vadose Zone.”

Information on the deep tensiometer was presented to the Arid Vadose Zone Alliance. The purpose of the meeting was to share lessons learned, to identify potential mutual technical support activities, and to develop this group to address science and technology gaps in arid vadose zone characterization, modeling, and monitoring.

Using deep tensiometers has been proposed for several DOE sites including the Savannah River Site, the Hanford Tank Farm, and the INTEC (INEEL) tank farm to assist in characterizing fluid movement in the vadose zone, delineating the presence and source of perched water and monitoring the effectiveness of disposal practices. A performance assessment monitoring plan was prepared for a disposal site at the Savannah River Site that proposes to install an array of vadose zone instruments, including deep tensiometers, in FY-99. Several deep tensiometers were installed at a test site at SRS.

An article entitled “Advanced Tensiometer for Water Potential Measurements” was prepared for the October 1998 issue of Measurements and Control magazine.

Several invention disclosures were submitted on instruments related to the deep (advanced) tensiometer. These instruments are a pore water piezometer, extensiopiezometer, and a tensiometer for agricultural applications. The pore water piezometer is an improvement on conventional piezometers used for engineering practices based on the deep tensiometer design. This piezometer has a faster response time than conventional piezometers. The extensiopiezometer is a combination extensiometer and piezometer to measure vertical consolidation and pore water pressure in either the saturated or unsaturated zones. The tensiometer for agricultural applications is a spin-off instrument related to the standard and deep tensiometers.

Deep tensiometers were installed at the Maricopa site by researchers at the University of Arizona to evaluate the potential for long-term monitoring in the vadose zone at disposal sites for the NRC.

Patent number 5,758,538 was granted June 2, 1998, by the U.S. Patent and Trademark Office for the deep tensiometer. The deep tensiometer is one of six technologies licensed to In Situ Inc. of Laramie, Wyoming, in FY 1997.

Design an integrated instrument array for monitoring subsurface biological processes.

Requirements for an integrated sensor for monitoring biologic processes in the vadose zone were defined. Conceptual designs were formulated to evaluate total biologic activity and nutrient availability in the vadose zone. These designs complement research conducted by doctors Colwell, Geesy, Gillis, and Lehman of the INEEL and Montana State University. Additional information on this development is available in Task 1.

TASK 4—Steam Enhanced Extraction in Fractured Porous Media.

Experiments were conducted that model steam condensation front propagation during the steam-enhanced extraction (SEE) process of removing liquid contaminants in fractured porous media. The process is being considered for implementation for removal of contaminants in the vesicular basalt flows that lie above the Snake River aquifer at the Idaho National Engineering and Environmental Laboratory (INEEL). The SEE process consists of steam injection into porous media that is unsaturated, or partially, or completely saturated with water and contains (typically) organic contaminants. The steam condenses, greatly reduces viscosity and surface tension of the contaminant, increases its vapor pressure, and this sweeps the contaminant in a condensation front toward a low pressure region established by a vacuum (and water) pump. Although the SEE process has been modeled and used successfully to remove contaminants in homogeneous porous media, such as sandy soil, the experiments are the first to model the process in fractured porous media.

The basalt flows of interest consist of a complex system of interlocking flow fingers and sedimentary interbeds about 1,000 m thick. Individual basalt fingers are typically 8 to 10 m thick. Features of the flow fingers that determine fluid flow distribution and resistance are highly fractured upper and lower vesicular (bubbly) regions, and a nonvesicular central region that contains widely spaced (on the order of 10 m) vertical fractures. The majority of fluid flow occurs within the vesicular regions. Because of the paramount importance of fluid transport through the fractured vesicular basalt regions for the steam-enhanced extraction process, the experiments are devoted to modeling the vesicular basalt regions.

A publication describing both experimental results and thermal analysis of condensation front propagation in unsaturated and saturated media has been prepared and is attached to this report (McCreery, G.E., and Martineau, R.C. “An Experimental Investigation of Steam Injection in Fractured Porous Media,” to be published, *Proceedings of the International Mechanical Engineering Congress and Exposition*, Anaheim, November 1998). The computer code PDEase is used to calculate matrix block temperature distribution and heat transfer adjacent to a propagating condensation front. A macroscopic energy balance method is presented that is useful for estimating energy and time requirements for the SEE process.

The SEE process in fractured porous media is dominated by condensation heat transfer to the matrix blocks. Because the time constants for heating the blocks may be larger than the transit time for the steam condensation front across the blocks, the process differs significantly from that in homogeneous porous material where local thermodynamic equilibrium may be assumed.

Initial observations concerning the SEE process in vesicular basalt flow include the possible (but not yet proven) advantages of:

- Thorough removal of volatile and semivolatile contaminants

- The possibility that contaminants may be removed from dead-ended pores. Other processes, such as vapor vacuum extraction, are expected to fail in this regard.

Possible disadvantages of the SEE process in vesicular basalt include:

- The process is energy inefficient due to very large ratios of heat transfer to the matrix compared with fracture fill material and contaminants

- The process may proceed unevenly through the fracture channels due to differences in thermal time constants of the matrix blocks and flow resistances of the channels

- The process may drive liquid contaminants downwards due to pressure gradient, gravity, and thermocapillary motion if well placement is not designed carefully

- Contaminant flow from the vadose zone towards the aquifer must be avoided.

In addition to the above paper, a poster was prepared and presented at the 1997 ASME International Mechanical Engineering Congress and Exposition. The reference is:

McCreery, G.E., and Martineau, R.C., “Visualization of Condensation Front position in Experiments Modeling Steam Enhanced Extraction of Contaminants in Fractured Porous Media,” Gallery of Heat Transfer session, International Mechanical Engineering Congress and Exposition, Dallas, November 1997.

Summary

The Steam-Enhanced Extraction in Fractured Porous media experiments and analysis have led to additional work implementing the M2NOTS (multicomponent, multiphase, nonisothermal organic transport simulator) code at the INEEL. The code is being used to analyze the SEE experiments. Preliminary calculations are in reasonable agreement with the data. Implementing the code has been a collaborative effort with Professor Kent Udell of the University of California at Berkeley.

TASK 5—Biologically Mediated Actinide Transport in the Subsurface: Saturated Zone Testing.

Moisture Content and Effective Reactive Surface Area: Conceptual Model Development

During FY 1998, a simplified model for estimating nonwetting (air) phase and wetting (water) phase relative permeability in porous media was developed and a manuscript prepared for publication. In this model, the porous media is represented by circular capillary tubes with solid circular rods inside the tubes; an annulus model. The grain size distribution of the porous media are used to establish the size of the capillaries and if a rod is placed in the annulus and what the rod radius is. Solution of the governing Navier-Stokes flow equations provides an estimate of the relative permeabilities. The model was applied to three data sets (sand, manufactured porous media, and sand plus gravel) and compared to the measured relative air and relative water permeability functions. A comparison is made for the sand data set between the modeled results and the results given by Brooks and Corey (1964) and Luckner et al. (1989). Though the Luckner et al. (1989) model, based on Mualem (1976), produces the closest fit (within 6% for 10% to 45% water saturation) to the sand data set, it requires the soil moisture characteristic curve be assessed first. The proposed model estimates relative air permeability (from 0% to 14% error for 10% to 60% water saturation) from the grain size distribution of the sand data set. The proposed model fits relative air permeability data for manufactured porous media with <5% for 0% to 100% water saturation and fits relative water permeability data for coarse sand and gravel data within <3% for 40% to 100% water saturation. This model represents the first step in establishing a theoretical relationship between relative permeability and wetted reactive surface area.

Microbially Mediated Uranium Transport in Saturated Aquifer Material:

The first year of research was primarily focused on setting up the radiological buffer area (RBA), obtaining, setting up and optimizing instrumentation, microbial enrichment, adsorption/desorption testing and preparation of column material for FY-99 research.

The RBA was set up in order to segregate the research using depleted uranium from other research occurring in the High Bay Laboratory. Due to the unique nature of the instruments required for the project and the necessity to limit the number of uranium containing samples leaving the RBA, instruments were required to be located in the RBA.

Analytical

Vials used to assay uranium sorption/desorption contained mineral salts, lactate, trichloroethylene (TCE), uranium, and sulfate depending on the enrichment specified. Lactate was monitored using high-pressure liquid chromatography. Trichloroethylene and associated reduction products were analyzed using gas chromatography (GC) using solid-phase microextraction (SPME) for sampling, while uranium was analyzed using a kinetic phosphorescence analyzer (KPA).

A GC sampling and analysis method was optimized using uranium free samples. During this time, the SPME sampling technique was optimized for the TCE concentrations used for testing. The primary purpose for using SPME for sampling was to decrease the amount of waste produced due to sample preparation for analysis.

The largest percentage of instrument optimization time was used for the KPA instrument. To increase the response from the KPA the plasma cartridge for the laser was changed to increase the intensity of the excitation beam. Following replacement of the cartridge, a short time course experiment was initiated to determine the effect of sulfate-reducing and methanogenic growth medium and test conditions on uranium analysis. In addition the experiment was designed to help determine analytical ranges and potential interference of test compounds for all of the equipment that will be used under real experimental conditions. Initial results indicated that chloride in the growth medium interfered with analysis for uranium using the KPA. The decision was made to switch to a growth medium consisting of only lactate, nitrate and phosphate. Sulfate will be added to the medium for enrichment of sulfate-reducing bacteria.

Culture Selection

Experiments were performed to understand the effect of carbon source on redox potential by microbial enrichments from TAN basalt or groundwater samples. Basalt from TAN 37 and groundwater from TAN 35 were used for enrichment of SRB and methanogens. TAN 37 is a deep monitoring well drilled in 1997 that is located approximately 150 feet east of TSF-05, the waste injection well. The TCE concentration in this area of the contaminant plume is approximately 400 ppb. TAN 35 is a monitoring well drilled in 1997 that is located approximately 700 feet east of TSF-05. The screened interval of the well begins at approximately 200 feet and bottoms out near 400 feet. The approximate TCE concentration in this area of the plume is 440 ppb. The experiments were performed to determine whether indigenous microbial communities from TAN could adequately reduce the media without the addition of an external reducing agent. Glucose and lactate were used as the carbon and electron sources for these experiments in an attempt to simulate experimental conditions used to study the accelerated anaerobic bioremediation of TCE-contaminated groundwater from TAN. Microbes from the groundwater were concentrated by filtering 500 ml of groundwater and then adding the filter to growth medium, while 3 to 4 g of crushed basalt was added to growth medium for enrichment from basalt. Microbial communities from the basalt and groundwater were enriched by adding sulfate to the growth medium or by growth medium without sulfate. Changes in redox potential were monitored using resazurin. Both sulfate-reducing and methanogenic microbial enrichments from TAN basalt using glucose as the carbon and electron source reduced the growth medium to a redox potential of less than –110 mV as indicated by the resazurin indicator in solution becoming colorless. Neither sulfate-reducing or methanogenic microbial communities from basalt receiving lactate as the carbon source were able to reduce the growth medium. Microbial communities concentrated from TAN groundwater reduced the growth medium to less than –110 mV within a few days using either glucose or lactate as the carbon and electron source whether enriched under sulfate-reducing or methanogenic conditions.

An inoculum from methanogenic enrichments from the groundwater were further enriched for SRBs and methanogens. The ability of these microbes to decrease the redox and the ability to convert lactate to other volatile fatty acids were compared to the ability of microbes used for TCE kinetic experiments (performed by Joni Barnes and Cathy Rae). The TCE kinetic culture was originally enriched from TAN-37 basalt and groundwater from TAN-29 a shallow monitoring well at TAN. The culture had been maintained by keeping sulfate levels in the culture similar to those found in the field (near 40 ppm sulfate). Using lactate as the carbon and energy source, the culture was able to reductively dechlorinate TCE to ethene and ethane. All of the cultures were able to reduce the medium to below –110 mV as indicated by resazurin and were able to convert lactate to acetate, formate, propionate, and butyrate. The cultures obtained from the TAN TCE kinetic experiments used lactate more slowly than the cultures enriched from TAN-35 groundwater. The slower lactate utilization patterns of the kinetic culture were thought to be better suited for the long-term adsorption/desorption experiments. For these reasons, we decided to use the TAN TCE kinetic culture for the rest of the testing.

Uranium Adsorption/Desorption Experiments

Approximately 270 serum vials were loaded with iron oxide-coated quartz to fulfill the first two objectives of the project. The objective of the experiment is to determine the effect of sulfate-reducing and methanogenic enrichment on uranium immobilization and mobilization from U-mineral oxide complexes on the surface of the quartz. Iron oxide-coated quartz is being used to simulate mineral surfaces on basalt, while enhancing the amount of uranium adsorption occurring due to the excess of reactive surface. For the initial experiment, the adsorption of uranium under reducing conditions established for TCE dechlorination was studied. This research task will help to determine the fate of soluble uranium during an active anaerobic bioremediation project. TCE was studied as the co-contaminant for the experiment. Two additional experiments used to determine the effect of adsorption time on uranium mobilization by methanogens and SRB have been initiated. Serum vials are being monitored weekly for U (VI), U (IV), TCE and associated products of reduction, and volatile fatty acids using the analytical instruments described above. Destructive sampling was used for analysis and samples were taken every week.

For the initial experiment, uranium (1 ppm) was added to growth medium containing lactate, phosphate and nitrate. A starting lactate concentration of 500 ppm was used for testing. The liquid was sparged with nitrogen to drive off excess oxygen and the vials were sealed. TCE and an inoculum were added to the vials to initiate the experiment and a time zero sample was taken. The calculated initial TCE concentration was approximately 12.8 ppm. A 10% inoculum from the TAN TCE kinetic studies culture discussed above was used for testing. The vials were incubated statically at room temperature. Five separate sets of vials were set up to monitor the effect of various test conditions on uranium adsorption. Each test consisted of SRB and methanogenic enrichments, a killed control containing TCE, a blank with TCE and a blank with no TCE. Blank in this instance is defined as the growth medium containing no inoculum. The killed control was used to determine whether biomass from the inoculum effected uranium concentrations in the liquid, while the blank was used to monitor uranium adsorption/desorption in the absence of cells or TCE. The TCE-containing blank was used to determine whether the TCE had any co-contaminant effects during the adsorption desorption process.

Lactate utilization for the SRB and methanogenic enrichments and the killed control can be seen in Figure 5. Lactate was removed in the SRB (Graph A) and methanogenic (Graph B) enrichments during the first 15 days of the experiment, while acetate in the medium rose to near 400 ppm and leveled off. Small amounts of other VFA were produced during the test. Lactate levels in the killed control (Graph C) remained near 500 ppm with the exception of the sample taken on day 30 in which growth was noted indicating contamination of the killed control. Figure 6 shows methane production from both the SRB and methanogenic enrichments. The cause of the initial methane spike in the SRB enrichments is not known. Visual examination of the cultures also indicated a black precipitate on the surface of the iron oxide-coated quartz in the SRB enrichments, but no precipitate on the quartz in the methanogenic enrichments. These results indicate that a mixed microbial population was present in the test mixture.

TCE removal by both cultures was negligible (Figure 7) which was initially surprising since the culture was able to reduce TCE to ethene and ethane during TAN TCE removal kinetic studies. The initial drop in the TCE concentration is attributed to sorption to the septum. The lack of TCE removal may have been due to the disappearance of lactate in the cultures after the first 15 days of testing. The culture required lactate to drive the dechlorination reaction (J. M. Barnes, personal communication).

The effect of the various test conditions on the U(VI) concentration in solution, as determined by KPA, can be seen in Figure 8. U (VI) concentrations are for filtered samples. Results indicate no U(VI) in vials containing either SRB and methanogenic enrichments. Disappearance of U(VI) was apparent in all of the conditions tested, but the blanks and controls showed U (VI) in solution. Disappearance of uranium from solution occurred until approximately day 23; following this time the uranium in the blank and killed control vials appeared to increase. Liquid samples from the blank and the methanogenic enrichment from the 30-day sample period were analyzed using the ICP to determine the amount of total U in unfiltered liquid. The samples indicated a total uranium concentration of 638 and 406 ppb uranium, respectively. These results indicate that a fair amount of uranium is present in solution in the U (IV) oxidation state. More research will be required to determine what is causing the reduction of U (VI) in the blanks. Due to the lack of availability or sensitivity of instruments such as x-ray photoelectron spectroscopy (XPS) and the scanning electron microscope, the surface of the iron oxide quartz has yet to be analyzed to determine the amount that has become chemically complexed to the iron oxide or the amount that may have precipitated on the surface within sulfides. Visual analysis of the iron oxide surface for microbes and precipitates will occur after the new environmental SEM and energy dispersive spectroscopy instrument has been placed online. Currently attempts are being made to verify uranium on the surface of the iron oxide-coated quartz by using secondary-ion mass spectroscopy (SIMS). Other methods of analysis that could potentially be used for analysis of the surface are laser ablation ICP.

A second set of batch tests to determine the effect of SRB and methanogenic enrichments on uranium desorption from iron oxide quartz are in progress. Experiments were initiated by adding a 1 ppm U (VI) solution to serum vials containing 1 g of iron oxide-coated quartz. The samples were allowed to stand for one month, followed by removal of the remaining uranium solution. The vials were then prepared for desorption tests by adding a nutrient medium containing lactate, nitrate, phosphate and sulfate, depending on the enrichment desired. The vials were then sparged with nitrogen to drive off excess oxygen and capped. The media was then inoculated with a 10% inoculum of the TAN TCE

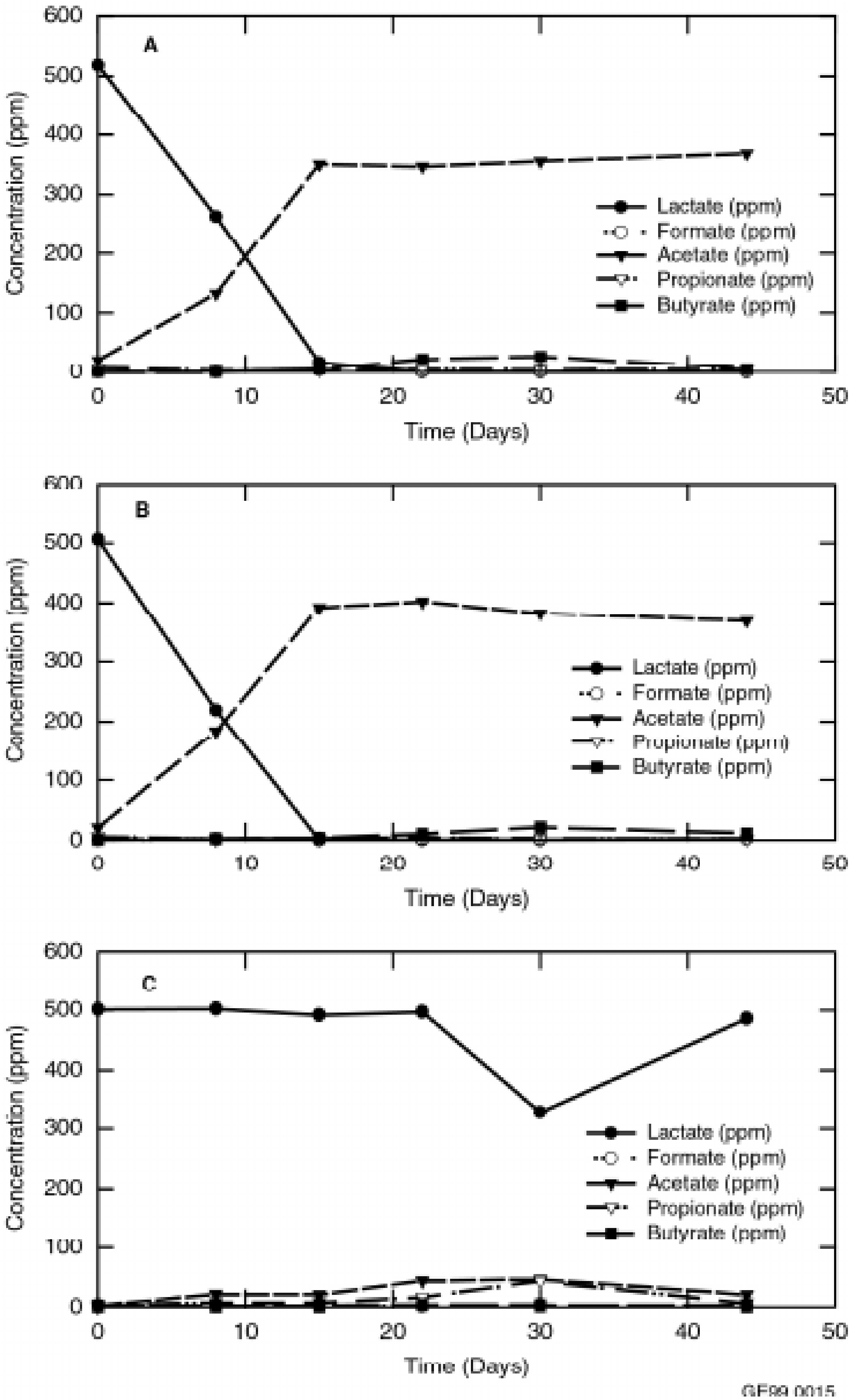

Figure 5. Lactate conversion in batch serum vial experiments to determine the effect of SRB and methanogenic enrichments no uranium adsorption to iron oxide coated quartz. (A) SRB enrichment, (B) methanogenic enrichment and (C) killed control.

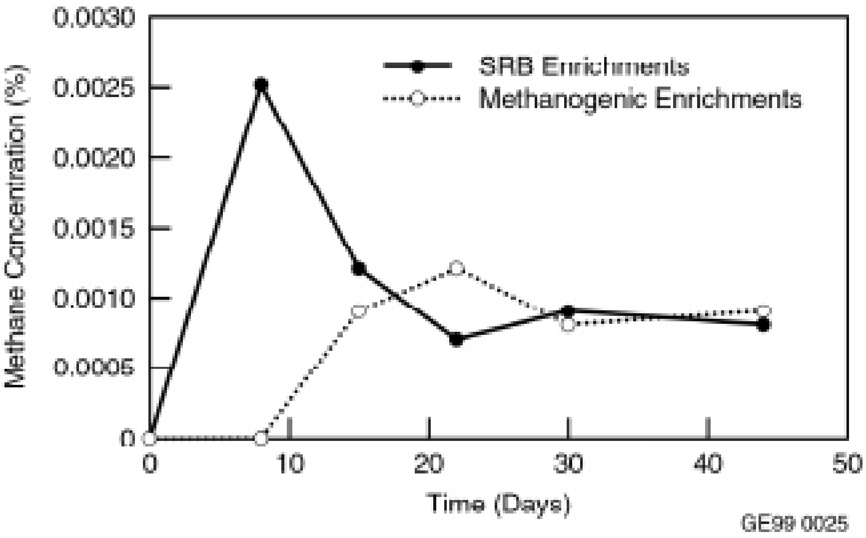

Figure 6. Methane production from SRB and methanogenic enrichments used to determine the effect of these enrichments on uranium adsorption to iron oxide coated quartz.

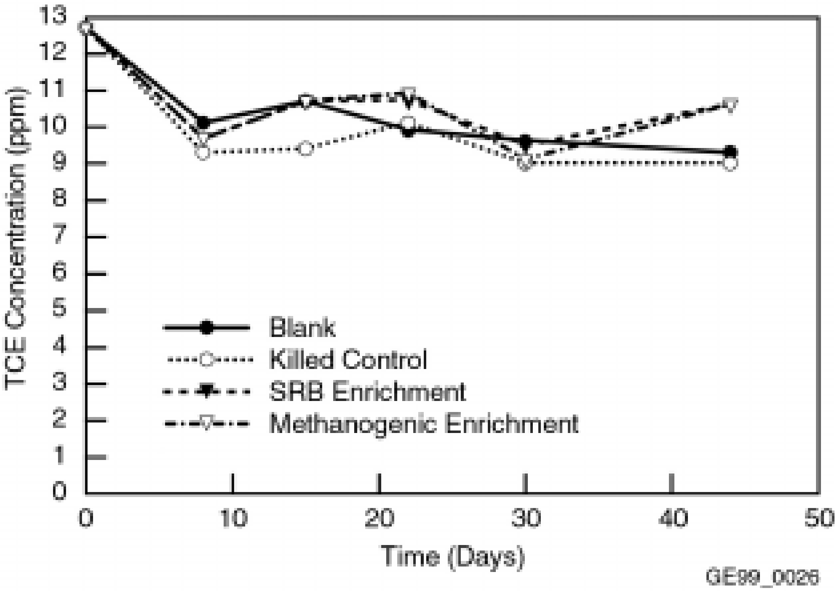

Figure 7. TCE removal from an experiment to determine the effect of SRB and methanogenic enrichments on uranium adsorption to iron oxide coated quartz.

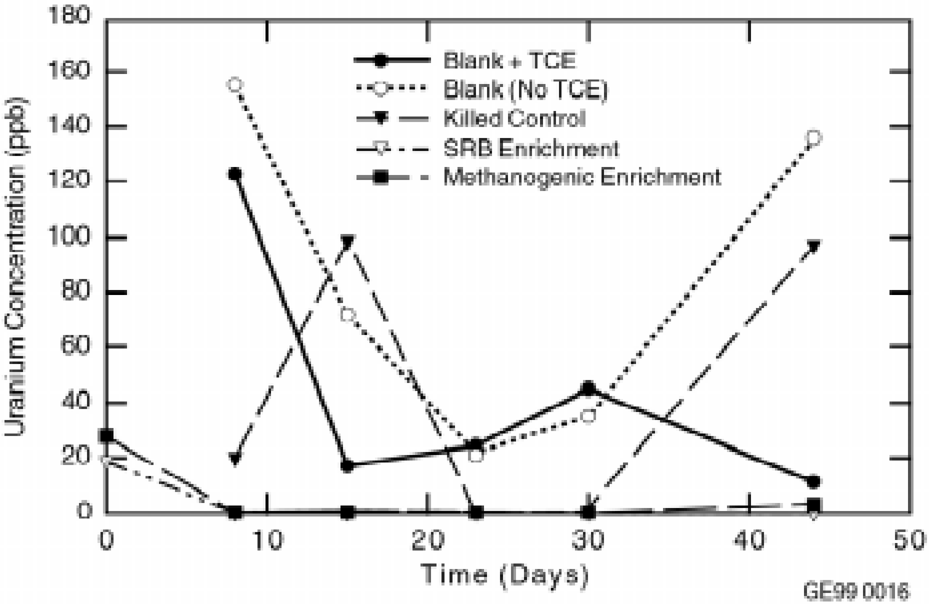

Figure 8. Concentration of U (VI) from an experiment to determine the effect of SRB and methanogenic enrichments on uranium adsorption to iron oxide coated quartz.

kinetic experiment culture then incubated statically at room temperature. As with the adsorption tests described above, five treatments were prepared for each sample point, SRB and methanogenic enrichments, blanks with and without TCE and a killed control.

Preliminary results from this test indicated a lactate utilization pattern similar to that demonstrated by the cultures during the adsorption testing. The SRB and methanogenic enrichments quickly removed the lactate and produced acetate, while the killed control removed no lactate. Methane production in both cultures was at levels similar to those demonstrated in the earlier experiment. Although the uranium-containing solution was aspirated from the system, a trace amount remained in solution in all the vials tested. After the system had equilibrated, the liquid in the vials contained between 120 and 140 ppb U (VI) with the exception of the blank with TCE and the SRB enrichment. The SRB enrichment contained less than 70 ppb U(VI). Differences between filtered and unfiltered samples indicated a significant amount of U(IV) in the form of filterable material. This indicated that the uranium either formed a colloidal solution or the microbes sorbed the uranium. Samples will be analyzed by ICP to determine the amount of total chromium in an attempt to differentiate between U(VI) and U (IV).

During the year the task of preparing basalt for column experiments during the next fiscal year were initiated. Basalt samples from TAN-33 a monitoring well containing approximately 700 ppb TCE located 1,300 feet east of TSF-05, were obtained for testing. The basalt sample came from a depth interval of 378 to 383 feet. The basalt was crushed to between 1/16 and 1/8” for testing. The basalt will be exposed to a 1 ppm U(VI) solution for approximately 3 months and then loaded into 2” x 12” glass columns.

Summary

The primary objective of the proposed research is to better understand the coupling of microbial processes and surface geochemical reactions that effect the migration of actinides such as plutonium and uranium through unsaturated and saturated zones in the subsurface. Two research thrusts are proposed to fulfill this objective; one related to vadose zone actinide migration and the other to saturated zone actinide migration. The first thrust is to derive relationships between sediment physical characteristics, moisture content, and biogeochemical reactivity. Laboratory research to understand the effect of anaerobic microbes, as well as the effect of oxidative conditions postremediation, on the mobility of uranium in saturated zones, which is the second thrust of the project.

During FY 1998, a simplified model for estimating nonwetting (air) phase and wetting (water) phase relative permeability in porous media was developed and a manuscript prepared for publication. In this model, the porous media is represented by circular capillary tubes with solid circular rods inside the tubes; an annulus model. The grain size distribution of the porous media are used to establish the size of the capillaries and if a rod is placed in the annulus and what the rod radius is. Solution of the governing Navier-Stokes flow equations provides an estimate of the relative permeabilities. This model represents the first step in establishing a theoretical relationship between relative permeability and wetted reactive surface area. Related to saturated zone actinide mobility, for FY 98 there were two primary objectives. The first was to demonstrate a link between anaerobic bioremediation of chlorinated contaminants and the obilization/immobilization of uranium from basalt and iron oxide minerals. The second goal of the research proposed was to understand the mechanisms responsible for the release of uranium from specific mineral components (e.g., iron oxide compounds) during anaerobic bioremediation. Batch serum vial experiments using iron oxide-coated quartz and SRB and methanogenic enrichments were used in an attempt to meet the above goals. Initial testing was performed to find a microbial population capable of lowering the redox potential of a nutrient medium without the addition of an external reductant. The tests were performed because a chemical reductant may adversely effect the adsorption/desorption and valence state of the uranium used for testing. Groundwater and basalt samples from TAN were used for enrichment. Cultures from groundwater and basalt were shown to be able to reduce growth medium to below –110 mV, a redox level considered anaerobic without the addition of a chemical reductant. A 1 ppm U (VI) solution was used for testing.

Initial results from the experiment demonstrate a potential link between adsorption of uranium to iron oxide-coated quartz. Assay vials containing SRB and methanogenic enrichments showed no U (VI) in the liquid indicating the reduction and possible precipitation of the uranium from solution, compared to blanks and controls showing uranium in solution. Due to the lack of sensitivity of the XPS instrument scheduled for use on the project for uranium, the reactive surface of the quartz particles has not been analyzed for uranium. Samples are being prepared for analysis on instruments that may be more sensitive for uranium, such as SIMS or laser ablation ICP. Once the new environmental SEM has been in operation, quartz samples will be viewed for microbial colonization and analyzed for iron, sulfur, and potentially uranium using EDS. Once these analytical instruments are optimized for use we will be able to determine the mechanisms responsible for uranium release from the U-mineral oxide complex. Iron oxide-coated quartz and basalt samples could potentially be analyzed using UV-VIS, fluorescence, and laser-induced fluorescence spectroscopy as well as other near-field microscopic techniques being developed through the Chemical and Biochemical Reactions at Environmental Surfaces Project within the Core Capabilities and Technical Enhancement Program. Using these analytical methods will potentially allow for determination of pH and redox potential at the interface where the microbes contact the U-mineral oxide complex.

The additional objectives/goals for the project are scheduled for completion during FY 99 and FY 00. These goals will be met using continuous flow column experiments. Columns will contain crushed basalt contaminated with uranium. The cultures used for the batch experiments will be added to the basalt and growth medium containing lactate, nitrate, phosphate and sulfate depending on the enrichment will be passed through the column in an upflow manner.

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COATINGS FOR ENVIRONMENTAL APPLICATIONS

R. N. Wright

Scope and Objectives

Thermal spray coatings can have an immediate, direct impact on the resolution of environmental legacy issues because they are used in diverse areas such as chemical reactors for supercritical water oxidation, thermal process equipment for waste vitrification and encapsulation, refurbishment of corroded storage tanks and barrels, and decontamination and decommissioning. In these and other applications thermal spray coatings improve the resistance of materials to thermal exposure, chemical attack, corrosion and erosion, and wear processes. In the broader sense of environmental surety, coatings can minimize or eliminate the use of processes that result in hazardous waste streams (e.g., chromium electroplating) while decreasing overall costs (e.g., corrosion-resistant coatings on carbon steel).

This project addresses plasma-sprayed protective coatings for high temperature process equipment for environmental management applications. The objective is to establish an understanding of the relationship of the in-flight particle characteristics (size, temperature, and velocity) to the microstructure and properties of the coating. In addition to the process variables, the role of surface preparation methods on residual stress and bonding will be examined for model ceramic and metallic coatings on steel substrates using numerical simulation and experiments. Methods will be developed to measure adhesion between the coating and the substrate, and the mechanical and physical properties of the coatings will be related to the processing conditions.

Technical Accomplishments

Background

Coatings are built up by the sequential impact and solidification of liquid or semi-solid droplets on a solid substrate. Droplets from powder or wire feedstock are heated and accelerated as they pass through a thermal spray system. Heating can be accomplished using combustion (e.g., flame spray or high velocity oxygen fuel systems), plasmas (e.g., conventional or high power plasma spray systems) or electric arcs (e.g., twin-wire arc systems). It has recently become possible to measure the size, velocity, and temperature of particles in real time during coating deposition. Particle temperatures just prior to impact may typically be several hundred degrees above the melting point of the material and velocities range from a few tens to hundreds of meters per second.

Despite the successful use of coatings in many engineering applications there is very limited scientific understanding of either the coating process or the resulting material properties. Typically an empirically determined recipe is developed for a particular coating application. The recipe specifies the type of thermal spray process, equipment control settings, and feedstock. If the conditions are varied, e.g., feedstock from another vendor is used, additional experiments are usually required to modify the process conditions to return the coating to the desired specifications. Coatings are generally inspected after the coating is completed, there is no on-line process control.

The relationship between the particle size, velocity, and temperature and the coating microstructure has been examined for a limited number of spray methods and simple model materials. To date the particle diagnostics have been more useful in explaining observed microstructures and properties than in prediction. It is also currently difficult to correlate the control parameters for the spray system (current, carrier gas, and mass flow rates for plasma spray for example) with the particle trajectories and residence times to predict the expected particle velocity and temperature.

Bonding between the coating and the substrate is not well understood; this is particularly true for coatings applied in the field to oxidized or corroded materials. Methods of surface preparation and the relationship to bonding have received little systematic study. Very little is known about novel surface preparation techniques like water jet or dry ice blasting that might be preferable to conventional grit blasting for environmental remediation activities to reduce or eliminate secondary waste production. The reliability of coatings in service is also difficult to predict. There is evidence that residual stresses induced during surface preparation and coating deposition can significantly influence the initial bonding and failure during service. The residual stresses are in turn related in a complex manner to the materials properties and processing conditions. As a result of the limited understanding of the coating process and material properties, there has been limited use of coatings in critical applications and there is a reluctance to specify coatings in many designs.

FY-98 Technical Accomplishments

Residual Stress

Residual stress is thought to be one of the major contributing factors to cracking and spallation of ceramic coatings. The total residual stress of the coating-substrate system is the sum of contributions of the stresses from difference in thermal expansion (referred to as the mismatch contribution) and quenching. Mismatch stresses arise when two bonded materials with different expansion coefficients are cooled. A compressive residual stress develops in the ceramic coating (which has the lower expansion coefficient) as it is forced to accommodate the greater thermal contraction of the higher coefficient metallic substrate, which has balancing tensile stresses. If the protective coating is applied by a thermal process, such as plasma spraying, quenching residual stress results as deposited hot material adheres to the cold substrate and rapidly cools.

There are a number of methods of measuring the residual stress in the coating, including x-ray or neutron diffraction. It is important for coating applications to measure the total residual stress in the coating-substrate system. During this year we developed a system that makes it possible to measure the total residual stress by measuring the curvature induced in thin metallic substrates by application of a coating using plasma spray. A schematic of the instrument is shown in Figure 1. A square array of 36 laser spots is reflected from the back surface of the substrate into a CCD video camera and the displacements of the spots due to curvature are determined from the video image using a software package that has been developed. The displacements are related to strain in the sample; strain can easily be converted to stress using Hooke’s Law for elastic deformation.

It is not possible to determine the quenching stress directly at this time, nor are the constitutive properties of the coating known. It is possible, however, to experimentally determine the mismatch component of the residual stress by observing the change in curvature of the substrate as a function of temperature. The laser measurement system shown in Figure 1, built for this program, is mounted on the outside of a vacuum chamber that is accessible to the laser through a quartz window. The substrate is resistively heated in the vacuum to allow these measurements to be made. A unique feature of the system is the noncontacting laser acoustic emission system that records changes in the coating material as a function of temperature. This system records changes that result from cracking or debonding between coating and substrate that might result in relaxation of the residual stress. The mismatch residual stress can therefore be accurately determined and the quenching contribution to residual stress is then easily calculated. The system will also allow observation of damage accumulation in the ceramic coating as a function of thermal cycling later in the research program.

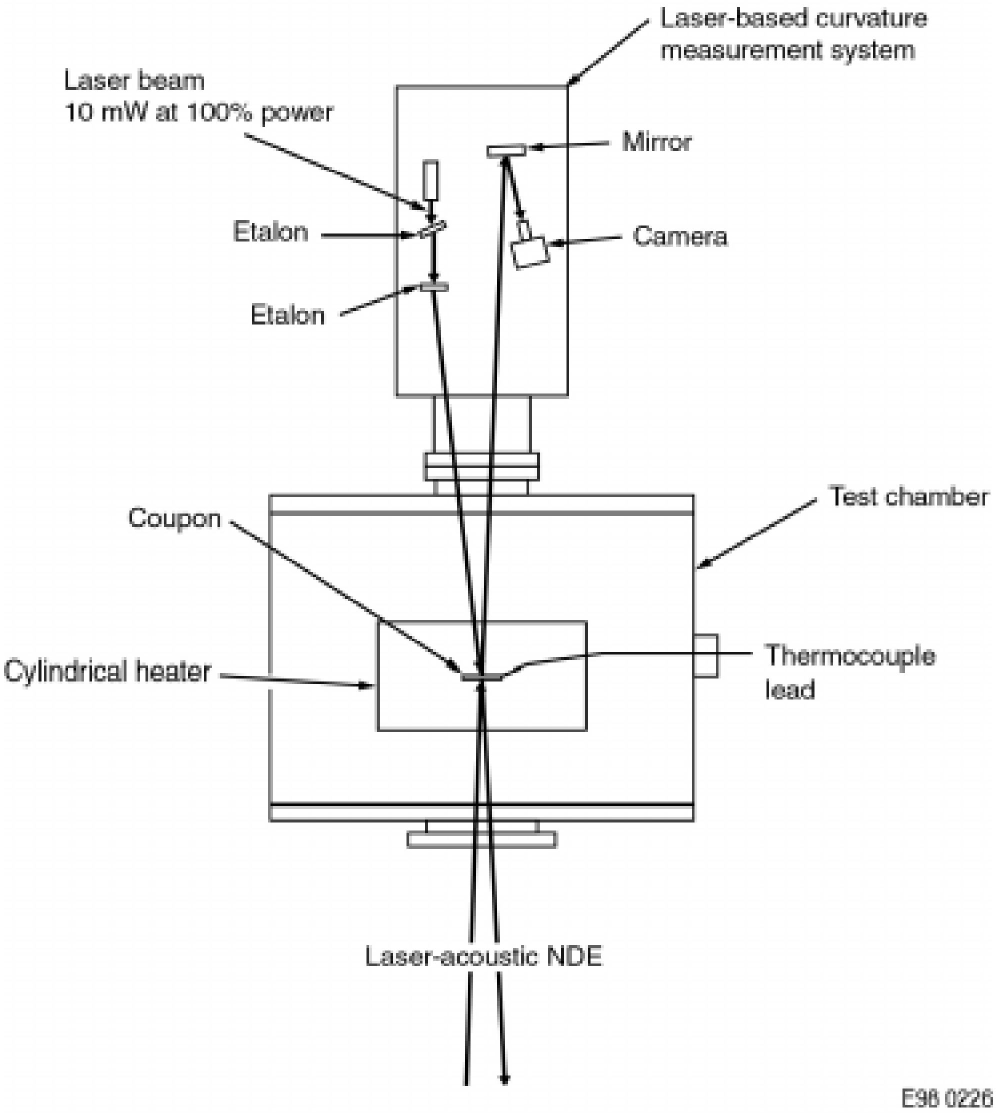


Figure 1. Schematic of the laser-based system that has been developed to measure the substrate curvature and thereby the total residual stress.

The mismatch stresses for a plasma sprayed spinel coating and a steel substrate were calculated using both analytic solutions and finite element modeling (FEM). This particular materials system was chosen because the bulk material properties are relatively well known and the ceramic does not undergo phase transformations on cooling. The results of these simulations should be generally applicable. Initially plate geometry was considered and FEM was used to determine that that temperature-dependent material properties and substrate plasticity have a minor effect, and the temperature independent fully elastic analytic solution gives an acceptable answer for this case. It was also determined that doubling the coating thickness from 0.76 to 1.5 mm on a 25 mm thick substrate causes only a slight decrease in compressive stress magnitude. The analytic solution for a coated rod was then derived and checked using FEM. Stress magnitudes are similar to the planar case, but vary throughout the thickness of the coating. In both cases a thick substrate and thin coating were assumed to be stress free at a temperature of 1000°C, and stresses were calculated as the specimen was cooled to room temperature.

Preliminary models of the quenching stresses have also been developed. Temperatures of a coated sample were calculated, both analytically and using FEM, assuming a 2300°C spinel temperature and a room temperature substrate. These calculated temperatures were much less than experimental measurements of similar plasma sprayed samples, indicating that convective heating from the plasma was dominant. Heat of fusion of the spinel was considered and determined to be insignificant. Therefore, the measured sample temperature of 450°C and the assumed spinel temperature of 2300°C were used to calculate the substrate temperature, which includes convective heating. These temperature changes were then used to calculate quenching stresses using FEM.

The capability to model experimentally-determined temperature histories of a sample as it is coated using a thermal spray process is also being developed. This is necessary for understanding the relative contributions of convective heating and cooling (for example the plasma flow and any forced air cooling), conduction and radiation, and also for calculating stresses that result from thermal gradients within a part. This capability will also be useful in exploring why coatings deposited in several thick layers behave differently than those deposited in many thinner layers when the total coating thickness is the same.

A complete understanding of the magnitude of residual stress and the factors that contribute to the two components of the residual stress will allow assessment of strategies to mitigate stress in engineering applications. For example, from the work conducted here it is clear that maintaining the substrate temperature at a minimum value will reduce the thermal contribution to the residual stress. It may be advantageous, however, to increase the substrate temperature by preheating or change the thickness of deposit developed in each coating pass (increasing the substrate temperature) to minimize the quenching stress by allowing greater relaxation of stress in the coating by creep or plastic deformation mechanisms. The analytical and experimental capabilities developed during the first year of this project allow such processing trade-offs to be systematically explored.

Adhesion

During this year we have also developed and applied the capability to measure the adhesion of coatings using standard ASTM methods. Coatings to be tested are applied to a specially machined threaded button using the same deposition parameters that are desired for coating application. The coated button is then bonded to a matching threaded button using one of several ASTM approved adhesives. The pair is tested in tension until the bond or the coating itself fails. Because of the nature of the test, the measured value of the adhesion can usually be thought of as a lower limit of the actual value. Note that while it is conceivable that the adhesive would fail before the bond or the coating, the adhesives used in the experiments have a tensile failure stress of approximately 75 MPa when applied according to the ASTM specification and this value is almost always higher than the failure strength of plasma-sprayed ceramic coatings. It is critical that there is no applied bending moment during testing to avoid a shear component of stress. Special spray fixtures and alignment fixtures were designed and fabricated for this project to ensure there is no shear stress when measured according to ASTM test procedures. This capability has been used, for example, to demonstrate that applying cooling air to the substrate can change the bond strength by a factor of two compared to an uncooled substrate.

Particle Visualization System and Laboratory Improvements

New instrumentation was acquired to enhance the diagnostic capabilities of the thermal spray laboratory. A laser strobe video system makes it possible to visually monitor and record the trajectory of particles through the plasma. The vision system uses a pulsed nitrogen laser to illuminate the particle flow field. The pulse width of the laser is 5 ns at a wavelength of 337 nm. These pulses are synchronized to a high-speed shutter of 50 ns duration. Both are synchronized to a CCD video camera frame rate of 1 to 30 frames per second. This temporal filtering, in combination with spectral filtering, results in an image that is free from the bright process light generated by the plasma arc. Particle injection into the 14,000°C plasma gases can now be monitored and controlled. Figure 2 shows a nickel alloy (NiCrAlY) powder being injected into a 30 kW argon/hydrogen plasma. This alloy is typically used as a bond coat to improve the adhesion between structural alloy substrates and ceramic coating materials. The particles are shown exiting the powder injection nozzle and entering the hot gas flow field vertically from above. They are rapidly redirected horizontally by the high velocity gases. Approximately 20 mm down stream those particles that remain in the gas flow field are heated to the point of vaporization as evidenced by the vapor trails coming off the particles in the direction of the plasma gas flow.

Visualization capability is significant for two reasons. Plasma spray guns are designed with a swirling gas flow field so that the arc attachment moves rapidly around the copper anode to avoid melting. This results in the particles exiting the torch with a complex flight path, such that one cannot assume that the point of spray deposition is coaxial with the centerline of the torch. In order to do precision deposition of a coating it is necessary to directly control the position of the center of mass of the particle flight path. More significantly, while we have previously developed the capability to measure the temperature and velocity of particles in flight, it is the interaction of the particles with the plasma that determines these parameters. It is possible, for example, that rather than increasing the particle temperature as one's intuition would suggest, increasing the torch power can decrease the residence time of particles in the plasma, with a concomitant decrease in the temperature. Similarly, it is also possible that increasing the powder feed rate (to increase the deposition rate) by increasing the flow of carrier gas can result in particle injection above the center of the plasma field. The result of the changes could be that the velocity and temperature of the particles are significantly reduced and the fraction of particles adhering to the substrate could be reduced, with the net result that a thinner coating is produced.

The existing thermal spray coating laboratory was modified. An additional spray station was added to the thermal spray laboratory to increase the efficiency of experimental setup and increase the capacity to handle simultaneous experiments. Developing environmental coatings requires a relatively large number of sample coupons for metallographic evaluation and corrosion testing; therefore, one of the spray stations is dedicated to coupon fabrication and the other is primarily used for diagnostic

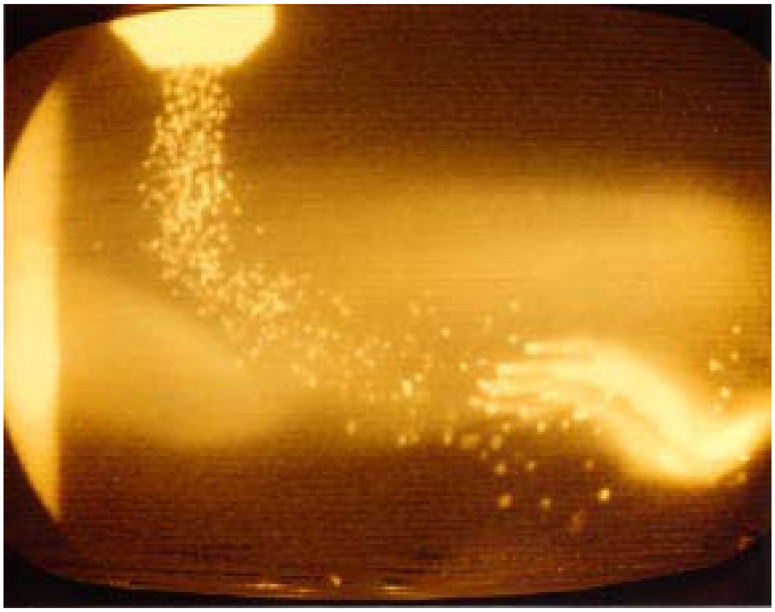


Figure 2. Laser strobe video image of NiCrAlY bond-coat particles injected into a 30 kW argon/hydrogen plasma. Particles are fed from the top and flow from left to right in the image.

measurements on the particle and gas flow fields. Solid spray particles that were previously discharged to the environment are now filtered with a new dust collection system. This system filters particles down to 0.5 µm in diameter with 99.995% efficiency. The new system also has more than twice the air flow capacity to protect workers and equipment from over-spray powder.

Summary

Coatings have wide applicability in environmental management and restoration activities, including high temperature processes for waste treatment and encapsulation, and refurbishing corroded storage systems. This project has developed new capabilities to establish a more scientific basis for relating the processing of coatings to their observed properties. Understanding the relationships between processing and the microstructure and properties of coatings will improve reliability, allow prediction of service performance in demanding environments, and enable new applications.

The first year of this project has addressed measurement and mitigation of residual stress in ceramic coatings deposited by plasma spray processes on structural steel. Residual stress is one of the critical factors in determining the resistance of ceramic coatings to fracture and debonding.

Capability to determine the two individual contributions, mismatch and quenching stresses, to the total residual stress has been developed through a unique instrument combining measurement of specimen curvature and laser acoustic emission techniques. Experiments have begun to relate the residual stress in the coating to the observed adhesive strength of ceramic coatings deposited with systematic variation in the process conditions.

Finite element methods have been developed to examine the development of residual stress in ceramic coatings as a function of the process parameters and deposition conditions. One component of the modeling has been development of a heat transfer model that is capable of accurately predicting the temperature gradients developed in a ceramic coating as the deposit thickness is built-up by successive passes from the thermal spray torch. Heat transfer from deposition of molten particles via conduction, and well as radiation and convection from the plasma, must all be incorporated to accurately describe heating in the coating-substrate system. The models have been validated with experiment. We have begun to examine the role of residual stress on the adhesion of near-full-density $MgAl_3O_4$ coatings on carbon steel substrates.

The ability to discriminate between the individual contributions to the total stress from thermal and quenching stresses, and the analytical capability that has been developed in this project, make it possible to suggest stress mitigation strategies for ceramic coatings. While technologically challenging schemes such as developing functionally gradient materials have been suggested previously, it appears from this work that stress mitigation in some systems might be aided by altering the initial temperature of the substrate, e.g., by preheating *in situ* with the plasma. Altering the cooling rate of the coating-substrate system from the maximum deposition temperature or changing the time at elevated temperature to allow stress relaxation by plastic flow or creep mechanisms will also be systematically explored.

CORROSION AND AGING

R. N. Wright

Scope and Objectives

Biologically induced or assisted corrosion has been reported, but little is known about the fundamentals of the process. This project is (1) examining the potential of microorganisms to establish biofilms on structural alloys that are significant to the interim and long-term storage of spent fuel and nuclear waste, and (2) carrying out fundamental studies of microorganisms in extreme environments that are representative of those of interest to DOE, i.e., high temperatures, pressures, and radiation fields.

Specific technical objectives for this task in FY 1998 included (1) construction of a genomic library of Sulfolobus, in which the complete genetic information of the organism is represented in a collection of fragments cloned in a reproducible array, (2) screening of that library for the presence of genes directing heavy metal resistance (specifically arsenic), (3) development of fluorescence *in situ* hybridization techniques to allow microscopic identification of the organism in mixed populations or environmental samples, (4) selective enrichment of the organism from environmental samples acquired in Yellowstone National Park, and (5) examination of growth behavior in a novel high temperature/high pressure bioreactor. Examination of new classes of microorganisms associated with the extreme environments of spent nuclear fuel storage began. Controlled experiments to determine the ability of organisms collected from extreme environments, as well as several controls using well characterized monotype cultures, to grow in gamma radiation fields similar to spent fuel storage environments will be carried out.

Technical Accomplishments

Background

Biofilms are microbial mats that adhere to the surface of nearly any substrate in natural aqueous environments. They have been found on fuel elements submerged in storage pools for spent nuclear fuel. Microbial cells attach to metals in an aquatic environment and initiate biomineralization reactions. Environmental conditions at the interface between the biofilm and substrate are radically different from the bulk medium in terms of pH, dissolved oxygen, and other organic and inorganic species. While there have been a number of reports of biologically induced or assisted corrosion, little is known about the fundamentals of the process, particularly the relationship between observed corrosion and the underlying heterogeneity in the metallurgical structure. The most significant microbiologically influenced corrosion occurs in the presence of microbial consortia, including sulfate-reducing bacteria, acid producing bacteria, metal-oxidizing bacteria, and metal reducing bacteria. Microorganisms are thought to influence corrosion by both dissolving and forming minerals. Passive layers on metals can be removed by biomineral dissolution reactions, leading to active electrochemical corrosion. The corrosion potential on metal surfaces can also shift as a result of biofilm formation.

It has recently been found that spent fuel plates in long term wet storage have significant biofilm growth. It has not yet been directly demonstrated, however, that the biofilms contribute significantly to materials degradation. One task of this project is to examine the potential of microorganisms to establish biofilms on structural alloys that are significant to the interim and long term storage of spent fuel and nuclear waste. The ability of microorganisms to initiate and accelerate corrosion in materials containing well-characterized heterogeneities (e.g., large second phase inclusions, welds, or cold work) will be examined. In addition to the potential for biological activity to accelerate corrosion in storage environments, there are more recent concerns that the biofilms may selectively take up radionuclides, which upon drying might become a significant source of particulate contamination during handling or transportation. The presence of biofilms, even in the absence of significant corrosion, is thus a potential concern.

Metallic coupons will be incubated under a variety of environmental conditions, including variations of temperature, water quality, and pH, with and without the inclusion of a suite of bacteria. A portion of the coupons will include autogenous weldments and welds made using typical filler metal alloys. Bacteria of interest include Deinococcus radiodurans (a well recognized radiation resistant microorganism), Thiobacillus ferrooxidans and Thiobacillus thiooxidans (chemolithotrophic species which attack sulfide minerals generating sulfuric acid), Acidiphilium spp. (acidophilic heterotrophic species), Ferromicrobium acidophilus (an iron-oxidizing, heterotrophic species), Pseudomonas aeruginosa (a neutrophilic, heterotrophic species frequently associated with biofilms in the environment). A range of anaerobic bacteria, including Clostridium spp. (fermentative anaerobes), Desulfovibrio, Desulfobacter, Methanosarcina, and Methanosaeta spp. (sulfate reducing bacteria and methanogens known to play a role in corrosion of metals) will also be considered. Biofilms formed will be analyzed to identify the species that have colonized the surfaces of the coupons and the coupons themselves will undergo surface analysis using a variety of techniques (e.g., optical and scanning electron microscopies, and electrochemical potential methods) to examine specific microstructural features that are susceptible to attack as a result of the biofilms.

A second task in this project is to carry out fundamental studies of microorganisms in extreme environments that are representative of DOE environmental concerns, e.g., high temperatures, pressures, and radiation fields. Microorganisms isolated from pristine, natural, extreme environments, as well as microorganisms associated with highly engineered and controlled environments, will be examined. This task is seeking to understand how these organisms survive, the range of extreme conditions they are able to tolerate, the mechanisms associated with survival under extreme conditions. This project was initiated at the INEEL in FY-97 with Laboratory Directed Research and Development funding and focused on fundamental questions concerning the biochemistry and genetics of the acidophilic, thermophilic bacterium Sulfolobus acidocaldarius. In mid-1998 the project was transferred to the Core Competencies program as a task within the Corrosion and Aging technical activities. The scope was expanded to examine the potential for the metabolic activity of these microbes to influence the stability of materials (such as spent nuclear fuel) stored in biologically extreme environments.

Biofilm Formation and Biocorrosion

Metal substrates chosen for these experiments are aluminum, stainless steel, and a zirconium alloy (representing fuel cladding). Metallurgical characterization of the as-received 6061-T6 aluminum, Type 304 stainless steel and zircaloy 4 coupons was carried out using optical and scanning electron microscopy. The grain sizes, both in-plane and through-thickness, were measured, and the nature and volume fraction of inclusions determined. The most notable observation was the presence of approximately 2.5% (by volume) of inclusions up to several microns in size in the 6061 aluminum alloy. The inclusions were found to consist of angular Fe_3SiAl_{12} and spherical Mg_2Si particles.

Two different sets of biocorrosion experiments are underway. The first is using glass incubation chambers to grow biofilms on metal coupons of all three compositions under a wide variety of water conditions. Three specific groups of bacterial are being used, acidophiles, sulfate reducing bacteria, and neutral pH organic carbon oxidizers. The purpose of these experiments is to screen a wide variety of conditions to determine which microorganisms are best able to form biofilms on metal surfaces with the minimal nutrients available from the water typical of storage pool environments. Biofilms are being allowed to grow under static conditions at a constant temperature of 30°C. Additional experiments are being conducted using dual component electrochemical cells that allow direct comparison between the biotic (with biofilm) and abiotic (nominally sterile) environments with identical water conditions at a constant temperature maintained by circulating water baths. A microporous membrane that allows electrolytic continuity without biological mixing connects two half-cells. Potentiostatic measurements are made periodically to determine the corrosion current and electrochemical potential between 6061-T6 corrosion coupons and standard measurement electrodes. The alloy, water chemistry, and type of bacteria were selected to yield the accelerated corrosion based on biofilm experiments.

Corrosion coupons that have been exposed to simulated storage pool environment have been removed from the corrosion tanks at regular intervals for biological and metallurgical analysis. The stainless steel and zircaloy coupons have not exhibited corrosion visible to the eye; however, the coupons show significant biofilm formation. An optical micrograph of bacteria making up the biofilm on a stainless steel coupon after formation of a mixed culture biofilm is shown in Figure 1. Observation of a biofilm on the zircaloy 4 alloy is significant since there were reports from very limited previous experiments that this material would not support biofilm growth.

Significant pitting corrosion, progressing by a grain boundary corrosion mechanism has been observed on the 6061 aluminum coupons. The 6061 alloy in the T-6 temper is usually thought of as being relatively resistant to grain boundary corrosion; however, the current observations are within the realm of typical behavior. Extensive characterization of the coupon material using transmission electron microscopy has shown that there is a precipitate free zone along the grain boundaries extending as much as 90 nm into each grain, shown in Figure 2. Precipitate free zones are known to occur in 6061 aluminum as a result of quench rates from the solution treatment that are toward the low end of the range allowed by specifications. Such inhomogeneities have been correlated with a propensity for intergranular corrosion. It should be noted that while the intergranular corrosion mechanism is specific to alloys with significant precipitate free zones at the grain boundaries, the occurrence of pitting is not correlated to the presence or absence of this microstructural inhomogeneity.

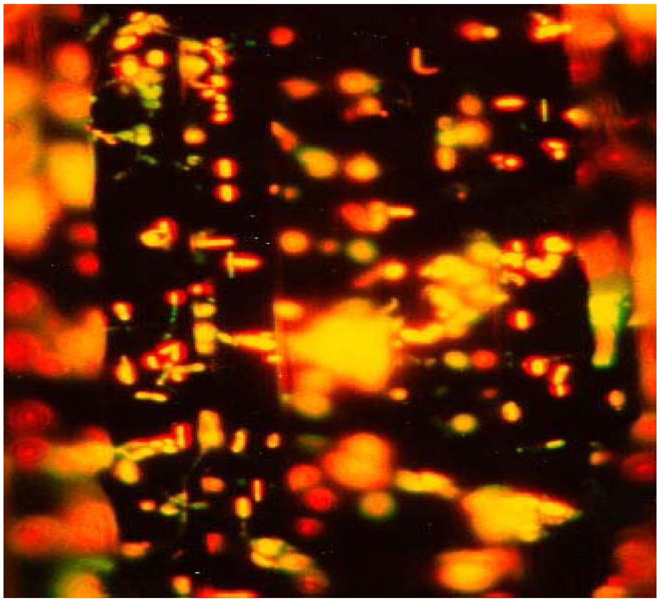


Figure 1. Optical micrograph of bacteria contained in the biofilm formed on Type 304 stainless steel.

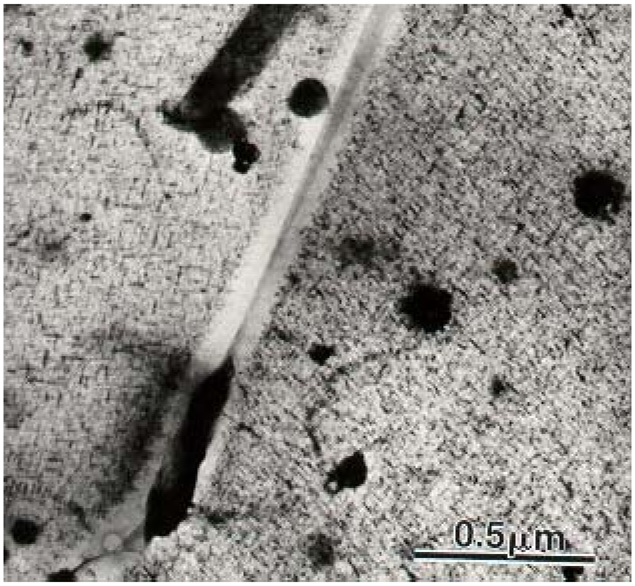


Figure 2. Transmission electron micrograph of precipitate free zone along a grain boundary in the 6061 T-6 aluminum used in the biocorrosion study. The fine "herringbone" pattern in the background is the precipitates that strengthen the alloy in the T-6 condition.

A scanning electrochemical microscope (commonly known by the acronym SRET) was obtained to conduct detailed electrochemical analysis of corrosion coupons with biofilms in an aqueous environment. This instrument uses a scanning vibrating probe technique to map the electrochemical potential differences on a microscale, which will enable local electrochemical cells beneath biofilms to be characterized in detail. Preliminary experiments have been carried out on reference specimens and 6061-T6 aluminum coupons containing pitting corrosion. The capability to map variations in potential on a scale comparable to the variations in surface topography resulting from preparation of the specimens (≈ 1–5 µm lateral spacing) has been demonstrated.

Microbiology of Extreme Environments

At its inception this project focused on the thermoacidophilic (literally, "heat and acid-loving") archaeon, Sulfolobus acidocaldarius. This microorganism was first isolated by Brock and coworkers in 1972 at Yellowstone National Park. The archaea have recently been confirmed by DNA sequence analysis of 16S ribosomal RNA genes to comprise a third major branch of life on Earth. They possess features (such as the ability to grow at temperatures at or above the boiling point of water) that suggest they could have thrived under conditions of the early Earth (hot, anaerobic, reducing environment). Whether or not the archaea in fact represent the oldest forms of life on Earth remains a subject of some debate.

Sulfolobus acidocaldarius was first reported to fix carbon dioxide and oxidize elemental sulfur as a sole source of energy and to also grow heterotrophically by oxidizing more complex carbon sources (such as sugars). More recent reports have indicated that the organism cannot grow autotrophically. An initial objective of this task was to obtain environmental samples from Yellowstone National Park to re-isolate this organism and establish unequivocally its metabolic range. To this end, samples were acquired from Moose Pool in Yellowstone, a thermal pool averaging 70°C with a pH of 2.0. A visible film of elemental sulfur was evident floating on the surface of this pool. Water samples were retrieved and inoculated into medias containing sulfur, iron, and pyrite. Growth observations were performed by periodic microscopic observation. The ability to metabolize sulfur would be of concern if it resulted in accelerated attack on the MnS inclusions that are ubiquitous in structural steels.

A novel high temperature/high pressure bioreactor was constructed during FY 1997. Currently it is being used to monitor the population dynamics of a mixed culture of thermoacidophilic bacteria resulting from introduction of a sample from Moose Pool.

Creation of a genomic library provides a reproducible source of DNA representing the entire DNA of an organism in an easy to handle format. The clones making up the library are arrayed in 96-well microtiter plates and frozen. The library can be easily replicated in a number of ways to allow screening for biochemical functions, as well as for the presence of specific DNA sequences. A genomic library of Sulfolobus acidocaldarius was constructed in the broad host range cosmid vector, pLAFR3. This vector carries the antibiotic resistance marker for tetracycline, and allows cloning of relatively large fragments of DNA (up to 30 kb) using bacteriophage lambda packaging mechanisms. Genomic DNA isolated from heterotrophically-grown S. acidocaldarius (overall genome size 2.8 million bp) was purified and partially digested with the restriction endonuclease Sau 3A, generating a collection of randomly-digested fragments. After size fractionation to enrich for fragments amenable to cloning in the cosmid vector pLAFR3 (10–40 kb), the pooled DNA was cloned into pLAFR3. Screening of the resulting cosmid library was performed using a regulatory gene sequence (arsR) from the bacterial arsenic resistance operon found in R773. Unfortunately, no homology to this gene sequence was found with the archaeal DNA library.

Aspects of the purification of Sulfolobus acidocaldarius using extinction dilutions and the application of fluorescence *in situ* hybridization (FISH) to analyzing Sulfolobus in culture and environmental samples were examined. FISH uses short (18-25 bp) fluorescently-tagged oligonucleotide probes targeting ribosomal RNA genes. Visualization of the probes is accomplished by epifluorescence microscopy. Highly specific probes can be designed that allow the microscopic distinction between different species of bacteria present in mixed populations. Specific techniques for applying FISH to Sulfolobus were developed. These included reducing the amount of sodium dodecyl sulfate used in hybridizing the probe to between 0.01–0.005% (reduced from the “standard” concentration of 0.1%), and examining slide preparations within 24 hr of sample fixation (cell suspensions on microscope slides are typically preserved by immersion in formalin solution for 1–24 hr prior to slide preparation). Conditions have been established for FISH, but cells produced in culture or in environmental samples have not yet been examined.

A portion of FY 1998 funding has directly addressed DOE-EM needs. Microbial corrosion of fuel element cladding is of special interest to the national spent fuel program, so we are investigating the microbial ecology of spent fuel storage pools. The chemical and physical environments of these pools may be considered extreme in terms of lack of nutrients and radiation (>10,000 R/hr).

Two sampling opportunities at INEEL interim storage facilities occurred in FY 1998. As part of routine corrosion monitoring, dummy Fermi canisters were retrieved and examined. Surface smears were taken for microbial analysis. These smears were transferred to liquid and solid microbial media that enrich for heterotrophic bacteria, acid-producing bacteria, and acidophilic and sulfate-reducing bacteria. Large numbers of heterotrophic and acid-producing bacteria were recovered from the enrichments, while no acidophilic or sulfate-reducing bacteria were observed. Bacteria were purified by repeated passage on solid media to select single colonies and unique representative colony morphologies were further analyzed using a 96-well nutritional assay (Biolog) to obtain species identifications. The dominant organism was a Gram-negative rod, producing copious amounts of mucoidal exopolysaccharide, provisionally identified as Pseudomonas putida (0.933 similarity index). Other unique Gram-negative organisms identified included Comamonas acidovorans and Gluconobacter cerinus (similarity indices of

0.843 and 0.811, respectively). A single Gram-positive species was identified as Corynebacterium aquaticum (similarity index of 0.648). This organism was distinctive in that it was highly pigmented (yellow).

Sampling of an older fuel storage pool occurred very recently, and while analyses are still underway, the results indicate a significantly higher diversity of microorganisms on the surfaces of metals in that facility. This is not surprising given that water quality is no longer controlled in this pool and that it was built to a lower standard, having unlined concrete walls rather than stainless steel lining. Preliminary observations indicate the presence not only of bacteria, but also of algae and diatoms.

The irradiation susceptibility or resistance of microbes living in environments representative of spent nuclear fuel storage will be determined. Microbes collected from INEEL spent fuel storage pools and standard monocultures will be exposed to a range of doses from 5,000 Rad to 100,000 Rad in Idaho State University's 6 MeV linear accelerator. The 5,000 Rad exposure will yield some indication of long term genetic effects of irradiation on these microbes. The 50,000 Rad exposure will give genetic as well as some somatic responses to the dose, and the 100,000 Rad exposure will indicate the potential somatic effect of these microbes for acute exposures.

Summary

The influence of biofilm formation on corrosion of structural materials that are important for long term storage of spent nuclear fuel is being investigated. The particular emphasis of the Biofilm Formation and Biocorrosion task is on the interaction of bacteria with heterogeneities in the 6061-T6 aluminum alloy, Type 304 stainless steel, and the zircaloy 4 zirconium alloy. Coupons with well-characterized metallurgical defects (e.g., intermetallic inclusions and weldments) are being exposed to aqueous environments with variations in water quality and several types of biota in long term experiments. We have established that biofilms form on all three types of alloy and that the 6061-T6 alloy exhibits extensive pitting corrosion. Electrochemical techniques are being applied to directly measure the local galvanic corrosion currents that result from the presence of biofilms with the intent of directly confirming the widely held belief that bacterial colonies cause accelerated corrosion.

Microorganisms tolerant of, or even thriving in, extremes of temperature, pH, heavy metals, pressure, and radiation, are termed extremophiles. Significant research and industrial attention is focused on such organisms. Environments found in operations across the DOE complex can be considered as extreme to most life forms, but may be suitable for microbial extremophiles that are thought to contribute to degradation of materials. The Microbiology of Extreme Environments task focused initially on Sulfolobus acidocaldarius, an organism that requires relatively high temperature (70°C) and low pH (<3) for growth. While oxidizing sulfur Sulfolobus acidocaldarius generates sulfuric acid, which can dissolve other minerals and metals in the local environment. Such an organism may play a role in attacking spent fuel cladding, where local surface temperatures may be elevated and sulfur contaminants may be used as an energy source by the bacterium. The presence of metal resistance genes (and expression of metal resistance) in this organism is being examined to identify mechanisms whereby this extremophile may also tolerate heavy metal-contaminated environments, as are common in some parts of the DOE complex.

A genomic DNA library for S. acidocaldarius has been constructed and screened for arsenic resistance genes. Enrichment of the organism from environmental samples obtained in Yellowstone National Park has been carried out. Molecular techniques to allow direct microscopic identification of Sulfolobus in environmental samples using FISH have been developed. We have also examined the growth of Sulfolobus in a novel high temperature and high pressure bioreactor.

Microorganisms from two spent nuclear fuel storage facilities at the INEEL have been purified and characterized. They are in the suite of biota used in the biocorrosion experiments. Experiments to characterize the radiotolerance of these bacteria, along with that of well-characterized monocultures, will be carried out using high-energy photons characteristic of the radiation fields expected in fuel storage environments.

TRANSPORT IN SOLID AND LIQUID MEDIA

C. Van Siclen

Scope and Objectives

Transport phenomena are a primary scientific concern of environmental and waste management. Examples include pollutant seepage through fractured rock to an underlying aquifer; spread of decay heat from buried radioactive wastes that may induce deleterious phase transformations in the containment material; flow of electrical current in waste vitrification; and diffusion and trapping of contaminant molecules in porous membranes. In every case, the flux occurs as a result of an applied field; these are connected by the transport coefficient, which in general is a second-rank tensor.

Calculation of the transport coefficient is the focus of this research project. This is a very difficult task because of the extreme sensitivity of the measured value of the transport coefficient to the *geometry* of the medium. For example, the tortuosity of the conducting paths through a conductor–insulator composite is the primary determinant of the effective conductivity of the material, while the actual volume fraction of conductor has lesser influence. Thus this research project must develop useful statistical descriptions of geometrically complex materials in addition to methods for calculating effective values for transport coefficients.

This project addresses the fundamental questions: (1) What is the relation between the transport properties of a material and its microstructure? (2) Can relations between different transport properties be found that are independent of a detailed description of the material? For FY 1998, the primary task was to develop a method to calculate "exact" values for transport coefficients of computer-generated composites, as this is needed for all the research that will follow.

Technical Accomplishments

The primary accomplishment over FY-98 is the development of the "walker diffusion method" for calculation of transport properties of composite materials. It produces "exact" values for transport coefficients from digitized images of real microstructures or computer-generated microstructures. However, as this method is computationally intensive, it will be most useful for evaluating the accuracy of (computationally much faster) statistical methods for calculating transport coefficients and of analytic, phenomenological expressions for the coefficients. The walker diffusion method is described briefly below. (Copies of a more detailed report submitted for publication are available through the program office.)

Transport phenomena arise from the occurrence of two vector fields, say $\mathbf{E}(\mathbf{r})$ and $\mathbf{J}(\mathbf{r})$, that satisfy the set of equations

$$\nabla\times\mathbf{E}=0, \quad \nabla\bullet\mathbf{J}=0, \quad \mathbf{J}=\sigma(\mathbf{r})\mathbf{E}, \quad \mathbf{E}=-\nabla\phi.$$

The quantity ϕ is a scalar potential, and $\sigma(\mathbf{r})$ is the local transport coefficient connecting the two local fields. When $\mathbf{E}$ and $\mathbf{J}$ are the electric field and the current density, respectively, σ is the electrical conductivity of the material. Other pairs of vector fields are connected by the dielectric constant ε, the magnetic permeability μ, the thermal conductivity κ, and the particle diffusion coefficient D. (Because the fluid permeability k appears in Stokes' equation instead, it cannot be obtained by the method presented here.)

Due to the commonality of the sets of field equations, a method that can solve for one effective transport coefficient can solve for the others as well. Thus consider a collection of non-interacting walkers. When a driving force $-\nabla\phi(\mathbf{r})$ is imposed, a diffusion current density $\mathbf{J}(\mathbf{r})$ is created, where

$$\mathbf{J}(\mathbf{r})=-D(\mathbf{r})\,\rho(\mathbf{r})\,\nabla\phi(\mathbf{r})$$

and $D(\mathbf{r})$ and $\rho(\mathbf{r})$ are the local walker diffusion coefficient and local walker density, respectively. As this diffusion equation resembles the transport equation above, the product $D(\mathbf{r})\,\rho(\mathbf{r})$ is identified with the local transport coefficient $\sigma(\mathbf{r})$. More specifically, $D(\mathbf{r})\,\rho^0(\mathbf{r}) \equiv \sigma(\mathbf{r})$, where $\rho^0(\mathbf{r})$ is the (local) equilibrium walker density in the absence of a driving force.

Thus a connection is made between a composite comprised of phase domains, each characterized by a transport coefficient value, and an isomorphic configuration of walker "domains" or populations, each characterized by values for equilibrium walker density and walker diffusion coefficient (see Figure 1). In analogy with the local relation above, the macroscopic transport coefficient σ equals the product of the average walker population $\langle\rho^0(\mathbf{r})\rangle$ of the isomorph and the diffusion coefficient D of a walker moving through the isomorph.

To maintain the equilibrium populations, the diffusing walker must obey the principle of detailed balance. This requires that the walker attempt a move in a randomly chosen direction during each time step, and that the move be successful with a probability that is a function of the local walker populations (so that a move from a less to a more populous domain is more likely than the reverse). This gives a relation between the time step and the (local) diffusion coefficient for walker diffusion within a domain.

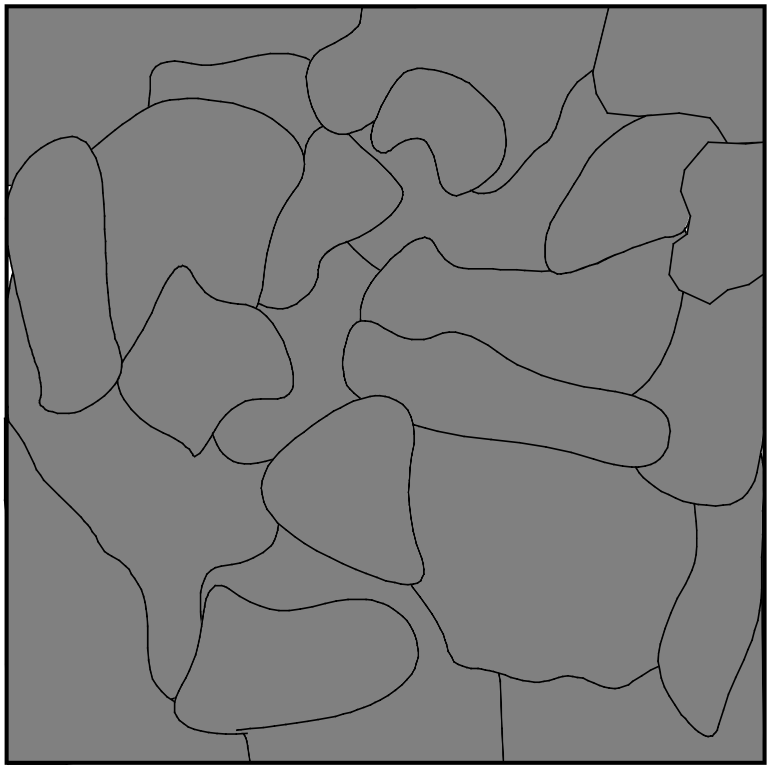


Figure 1. Multi-phase composite comprised of phase domains distinguished by shade of gray. Alternatively, this structure may be regarded as a composite isomorph comprised of walker populations.

A key insight is that the local diffusion coefficient for the walker should be constant throughout the composite isomorph. This causes the walker trajectory to fully reflect the microstructure *geometry*, as only the domain boundaries can then affect the walker behavior. A further consequence is that the walker populations $\rho^0(\mathbf{r})$ are identified with (i.e., have the value of) the transport coefficient $\sigma(\mathbf{r})$ for the corresponding phase domains. Thus the macroscopic transport coefficient $\sigma=\langle\sigma(\mathbf{r})\rangle D$, showing that the geometric aspects of the microstructure are completely accounted for in the walker diffusion coefficient D. The value D is straightforwardly calculated from the total displacement of the walker over the time corresponding to the number of attempted moves.

This is a remarkable result. By the "trick" of relating composite phase domains to (imaginary!) walker populations, a simple expression for the macroscopic transport coefficient has been found; this is the product of the average value $\langle\sigma(\mathbf{r})\rangle$ of the local transport coefficients taken over the entire composite material, and a parameter D that contains all the geometric information about the material. As mentioned above, this method for calculating effective transport coefficients can be applied to a three-dimensional, digitized image of a real microstructure. The accuracy of the calculated value for D will of course increase as the walker visits a larger volume of the digitized image.

The diffusion procedure described above is computationally inefficient since not all attempted moves by the walker are successful. This is overcome by *averaging* the behavior of the walker over time such that every attempt is successful but the move is accomplished over a variable time interval. In this "variable residence time algorithm," the direction of each move is determined randomly from a set of probabilities that are functions of the local walker populations, and the move occurs over a time interval that is similarly a function of the local walker populations.

To verify the walker diffusion method and the variable residence time algorithm, two important results from percolation theory were reproduced. The first states that the effective conductivity σ of a two-dimensional, two-phase disordered composite at the percolation threshold p_c of the higher-conductivity phase A is related to the conductivities σ_A and σ_B of the two phases by the equation $\sigma/\sigma_A \propto (\sigma_B/\sigma_A)^{1/2}$. In this case, the percolation threshold is that a real fraction $\phi_A=p_c=0.59275$ of phase A such that a single continuous path of phase A spans an infinitely large composite. Figure 2(a) shows a 200×200-site region of such a two-phase disordered composite. Numerical results are presented in Figure 2(b) along with a "best fit" straight line having slope 0.5005±0.0025 to compare with the predicted critical exponent of ½. Interestingly, the y-intercept of the line is not zero, reflecting the preference of the walker for the higher-conductivity regions that are inevitable in imperfectly random systems.

The second result from percolation theory states that the effective conductivity σ of a disordered conductor–insulator system goes to zero like $\sigma \sim (\phi_A - p_c)^\mu$ as the conducting phase volume fraction ϕ_A approaches p_c from above. In fact, the numerical results presented in Figure 3 for two-dimensional systems show that this relationship holds for all $\phi_A > p_c$. The "best fit" straight line has slope $\mu=1.2534\pm0.0053$, in good agreement with the experimental value of 1.28±0.05. The leftmost point in Figure 3, which was not included in the fit, lies well off the straight line due to the increasingly fractal character of the conducting domains as ϕ_A approaches p_c. Walker diffusion on a fractal domain is "anomalous" (non-Gaussian) and cannot be related to transport properties. Each data point in Figure 3 represents thirty calculations of the walker diffusion coefficient D; each calculation took roughly three hours on a dedicated 500 MHz DEC Alpha workstation.

The variable residence time algorithm has also been used to derive a "random medium" approximation (RMA) for transport coefficients of disordered composites that may be an improvement over the standard effective medium approximations. Of particular interest is the fact that the RMA reduces to $\sigma/\sigma_A=\phi_A^2$ for a disordered conductor–insulator system. This expression is Archie's Law with a

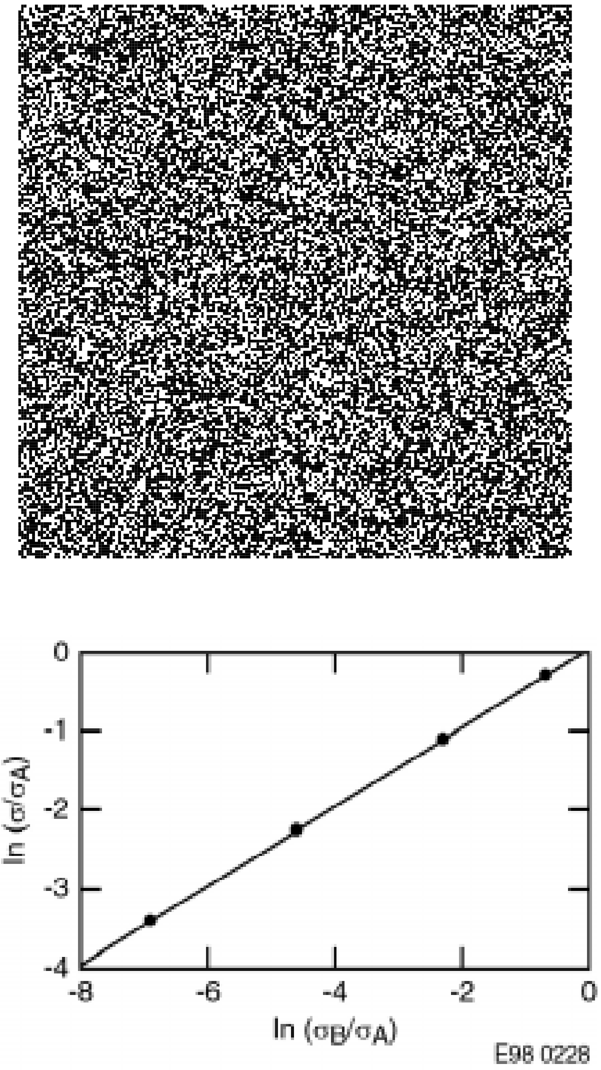


Figure 2. (a) Two-dimensional, two-phase (black and white) disordered composite in which (black) phase A has volume fraction $\phi_A = p_c$ and conductivity σ_A, and (white) phase B has volume fraction $\phi_B = (1 - p_c)$ and conductivity σ_B. (b) Calculated values of the conductivity ratio σ/σ_A of such composites. The four data points are taken for $\sigma_B/\sigma_A = 0.5, 0.1, 0.01$, and 0.001.

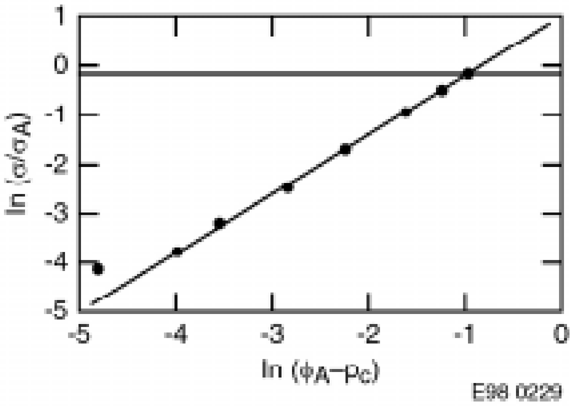


Figure 3. Calculated values of the conductivity ratio σ/σ_A of two-dimensional, disordered conductor-insulator systems, where the conducting phase has conductivity σ_A and volume fraction ϕ_A. The eight data points are taken for ϕ_A = 1.0, 0.9, 0.8, 0.7, 0.65, 0.62, 0.61, and 0.60.

cementation index of 2, which is well known to describe the conductivity of porous rock (σ_A is then the conductivity of the fluid that fills the pores).

Work-in-progress includes a study of diffusion through fractal structures. This is not an esoteric exercise: sandstones are fractals (the pore space is a volume fractal and the pore–grain interface is a surface fractal) at length scales up to the average grain size and homogenous at length scales above that; cracks in rock often show a logarithmic length distribution, and crack faces are typically fractal. The transport properties of rocks must surely reflect their fractal nature.

An analytic derivation gives the relation $D \sim \xi^{2-d_w}$ between the macroscopic walker diffusion coefficient D, the length scale ξ at which the material changes from fractal to homogeneous, and the fractal dimension d_w of the walker trajectory through the fractal structure. Interestingly, this relation leads to Archie’s Law with a cementation index between 2 and 3 for the case of sandstones, in reasonable agreement with experiment. [The trajectory dimension d_w can be related to the fractal dimension(s) of the material structure, which in turn can be determined for real samples by image analysis.] However, this relation remains to be confirmed by calculations (using the walker diffusion method) on computer-generated fractal structures. In addition, it will be interesting to see whether the walker trajectory through a multi-phase (rather than conductor–insulator) fractal structure is fractal.

Summary

The walker diffusion method has been developed for calculating “exact” values of effective transport coefficients for arbitrarily complex microstructures. Because the walker trajectory reflects the geometry (phase distribution and phase domain morphology) of the microstructure, this method additionally provides insight into the relation between the transport and geometric properties of the material. Other work includes an on-going study of the transport properties of fractal structures; an important initial result is a relation between the transport coefficients and the fractal dimension of the walker trajectory through the structure. Clearly the concept of an imaginary walker exploring a microstructure has proved to be fruitful.

ANALYZING AGING DOE FACILITIES EXPOSED TO NATURAL AND MAN MADE ENVIRONMENTAL INFLUENCES

N. M. Carlson

Scope and Objectives

This task addressed the need to develop a research-based life-cycle management engineering model that will provide INEEL and DOE with a tool for estimating life-cycle costs for INEEL structures. Roof systems present one of the most common repair/replace expenses at all INEEL facilities, so roofing systems were the focus of this task. The roof management life cycle engineering model would establish a relational database specific to the INEEL, providing guidance to designers, inspectors, facility managers, and operations personnel in making roof system choices based on INEEL weather, materials issues, facility use, facility design, and prior inspection data. The model design permits updating of all input data as more accurate data become available.

To establish input data available and materials research required for the INEEL life cycle management-engineering model, the following research objectives were established for FY-98.

- Determine the primary degradation mechanisms for single ply, built up, and metal roofing systems at the INEEL.
- Prepare a summary report detailing degradation mechanisms by roof system type, current INEEL roof management practices, and the need for, as well as the benefits of, a research based life cycle management engineering model.
- Disseminate the report results to INEEL and DOE-ID facility and operations management personnel.
- Develop a technical resource library of text detailing materials properties, degradation mechanisms, and durability testing specific to roofing systems.
- Acquire a freeze/thaw chamber for testing 4’ × 4’ roofing.
- Establish commercial software availability and suitability for use in the INEEL life cycle management-engineering model relational database.
- Obtain National Oceanic and Atmospheric Administration (NOAA) data from INEEL weather stations for use in the relational database.
- Collaborate with and guide research efforts at Massachusetts Institute of Technology (MIT), Department of Civil and Environmental Engineering, to develop a research summary on roof system degradation mechanisms.

Technical Accomplishments

Background

DOE-ID has stated the need for effective management of INEEL facilities in ID N 430.1A, “Life Cycle Asset Management: ID Expectations.” Roof systems are one of the most common sources of repair/replace expenses at all INEEL facilities (INEEL has over 4,000,000 ft^2 of roofs on more than 550 buildings). Thus roofing systems were identified as the initial focus of the engineering modeling effort. Commercially available roof system management software can provide roof conditions based on visual inspection reports, and some packages provided projected repair costs based on the roof condition. However, past experience at the INEEL indicated that roofing decisions based primarily on initial cost rather than life-cycle cost have resulted in roofing system choices that were not always the most appropriate based on facility use, materials incompatibility, materials degradation factors, maintenance practices, and environmental factors. The roof management life cycle engineering model being developed will relate, at a minimum, INEEL NOAA weather data, materials durability issues, facility use, degradation processes, and historical INEEL roof inspection data as these data impact life-cycle costs of candidate new or repair/replace roofing systems. The roof management life cycle engineering model will focus initially on INEEL single ply, built-up (BUR), and metal roofing, which account for 93% of the roofs at the INEEL; Figure 1 lists all the roof types found at INEEL.

At present, a system named ROOFER is used to evaluate the single-ply and built-up roofs and effectively manage these roofing systems. ROOFER was developed by the U.S. Army as a systematic method to determine a repair strategy for bituminous built-up[1] and single-ply[2] roofing systems. Inspection reports are input when evidence of roofing problems are manifested by water infiltration effects observed in the building. The ROOFER system uses visual inspection data on the condition of the roof membrane, flashing, and insulation to calculate a roof condition index rating for an entire roof or a section of a roofing system. The ROOFER software can also generate a corrective action plan that can be used for bids if a repair/replace decision is made based on the roof condition index. The ROOFER software does not provide life-cycle cost estimating information for use in management decisions nor are the results of inspections and ROOFER data consistently used by facility managers in making repair/replacement decisions. Furthermore, materials science research into materials properties, materials interactions, and materials durability in the arid, high mountain climate of Idaho is required to establish research based materials properties rather than relying on research results reported by the manufacturer on candidate roofing system materials. The INEEL engineering model, with appropriate modifications, could be used at other complexes throughout the DOE providing enhanced facility management practices, more cost effective use of federal dollars, and structures in which critical DOE-EM activities can be completed without facility related disruptions.

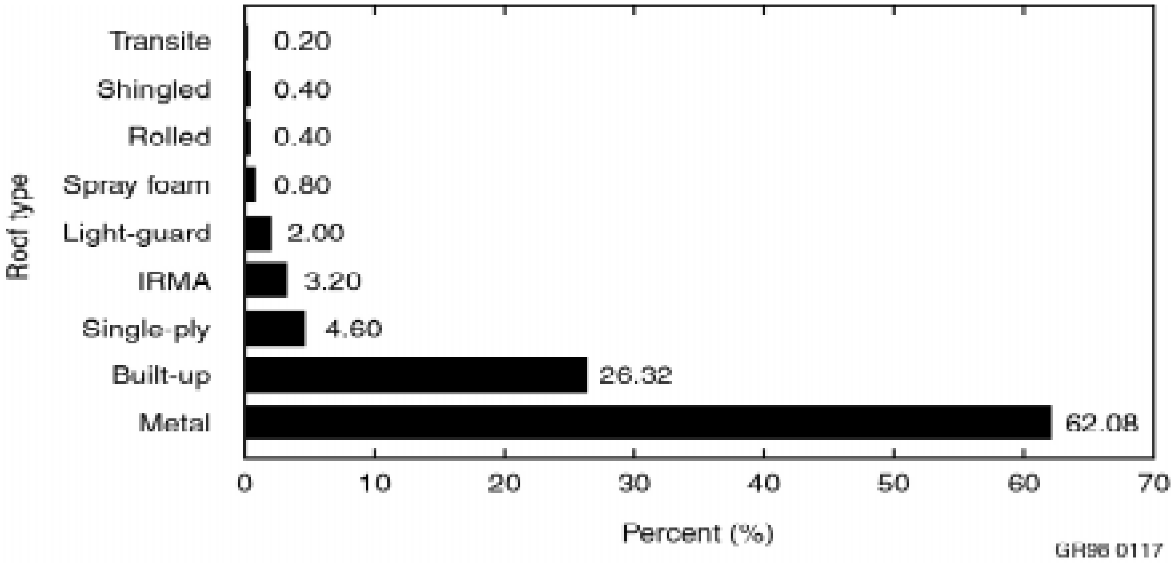


Figure 1. INEEL roof types, by percent.

FY 1998 Technical Accomplishments

Understanding Roofing Systems

To determine the materials properties and degradation mechanisms for single-ply, built-up, and metal roof systems, members of the research team, including MIT, researched the available literature. Three team members attended the Roofing Industry Educational Institute (RIEI) class on "Architectural and Low Slope Metal Roofing Systems," as 62% of the roofing systems at the INEEL are metal and not currently covered by the ROOFER program. (The ROOFER software is to be expanded in the next few years to include metal systems.) Class attendance provided the researchers with an understanding of materials concerns relating to metal roof systems as well as an understanding of metal roof distress types inspectors will need to assess for input to ROOFER.

The reader is provided with a brief description of each roof system to provide a better understanding of materials issues relating to each roofing system. The description is excerpted from an RIEI Information Letter article entitled "Understanding Roofing Systems."[3]

> INTRODUCTION
>
> To help sort the various roofing systems available, we are separating them by either multi-ply or single ply. The multi-ply systems generally are bitumen (asphalt or coal tar) based, while single ply includes the polymer and metal systems.
>
> MULTI-PLY SYSTEMS
>
> BUILT-UP
>
> *Description:* Historically, the most common low-sloped roofing type. These systems are "built-up" from alternating layers of roofing felt and asphalt or coal-tar. The reinforcing felts of yesterday were made from recycled rags and paper or asbestos. Today, the vast majority of these roofs use fiberglass as the reinforcing felt. The roof functions by having the felt reinforce thin, uniform layers of waterproof bitumen.
>
> Built-up roofing commonly uses descriptions based on how many layers of roofing felt are overlapped (i.e., 3-ply, 4-ply). The waterproofing factor is determined by the bitumen layers and not the felt. Therefore, if you have 3 plies of felt (the minimum number of plies), there are two or more waterproofing layers, depending on the method of attachment of the membrane to the substrate and the top coating used. The felt provides the strength to resist thermal and other rooftop stresses. The system is adhered to the top of an insulation layer, or to a base sheet, that is fastened to the roof deck.
>
> *Ideal application:* Owner-maintained facilities usually use built-up roofing. These roofs can be maintained by in-house staff with some training. Repair materials are readily available and the techniques are not difficult to master. Built-up roofs are reasonably abuse-resistant and difficult to vandalize.

Potential problems: The smell during installation can be very disruptive. However, today there are fume control kettles available that greatly reduce the fumes and odor. Supervision of installers is recommended, because it is difficult to detect if shortcuts were taken once the roof is installed.

MODIFIED BITUMEN

Description: The waterproofing abilities of asphalt and coal-tar can be compromised when made into moppable roofing grades. Therefore, the use of polymers to modify or change the properties of asphalt so that it will be stable at a wide range of rooftop temperatures has become a popular option. This modified bitumen is put onto a reinforcing carrier, cooled and rolled-up, creating a waterproof/ weatherproof sheet. These sheets are then assembled into the final roofing product.

Asphalt modified with either Styrene Butadiene Styrene (SBS) or Atactic (Amorphous) PolyPropylene (APP) on a reinforcing carrier are the traditional materials used. The material can be attached by mopping (SBS), torching it in place (APP or SBS), or using special cold adhesives designed for the specific system (SBS or APP). There are some self-adhering systems available (SBS).

Ideal application: Modified roofs are very versatile. They can go onto most buildings that have good drainage. They are tough and, when damaged, not too difficult to repair using cold repairs like BUR or torching. These systems are cost effective on most buildings, especially those with a lot of flashing.

Potential problems: Open torches on the roof top create a fire risk. Also, like most systems care and correct application is necessary, so the installation crews need to be knowledgeable about the system being installed.

SINGLE-PLY

EPDM

Description: Large sheets of synthetic rubber that are unrolled on the roof and seamed in place using adhesives or special tapes. The roof is complete in a single layer, thereby the term “single-ply.” The rubber used to make the large sheets is Ethylene Propylene Diene Terpolymer (EPDM) - a highly-weather-resistant, synthetic polymer designed for thermal stability and blended with carbon black, oils and other additives.

EPDM membranes are anchored to the building using one of three techniques: Ballasted is the most common and uses stone or concrete pavers that will resist the potential for the roof to blow off. The membrane is laid over non-anchored insulation boards. The membrane is seamed together and covered with a minimum of 10 pounds per square foot of nominal 1-1 /2” rounded river-bottom stone.

Mechanically attached systems use rows of fasteners to hold the membrane to the roof deck. Wind and thermal forces are transferred from the membrane to the fastener and, ultimately, to the deck. These systems vary greatly from manufacturer to manufacturer.

The last anchoring technique involves Full adhered, which uses either a contact adhesive, sprayed foam or asphalt to attach the rubber to the top of an insulation layer. The adhesives used contain solvent, so any air intakes near the work area should be closed off to reduce the amount of solvent fumes in the building.

Ideal application: EPDM is best suited for roofs with vast, open areas where the large panel size allows fast installation.

Potential problems: A major concern with rubber roofs is cuts/tears; another is seams. In addition, ballasted roofs, with their thick stone cover, are hard to inspect and it is difficult to detect leaks. It is recommended that walkways be provided to allow easier movement across the roof.

THERMOPLASTIC or WELDABLE

Description: Thermoplastic sheets are heat-welded, with hot air used to create a seam by fusing the separate pieces of sheet together. These sheets are manufactured from thermoplastic resins, the most common being PVC and TPO. They are reinforced with either a fiberglass or polyester scrim.

Thermoplastic systems are. most often mechanically attached to the deck through the lap area. This lets them take maximum advantage of their light color and scrim reinforcement. The seams when properly done are as strong as the sheet itself.

Ideal application: On roof decks that will take a fastener, where good fire resistance is needed, and where concerns about seams are an issue. These systems are also puncture-resistant, as well as highly resistant to certain chemicals.

Potential problems: These materials are very slippery when wet. On sloped roofs, walking can be dangerous if the roof is wet. The earlier versions of some of these products suffered premature failures, that today’s products over come.

METAL

Description: There are two basic types of metal roofing: architectural and structural. The difference between them is that architectural systems need the metal to be supported on a continuous deck; while structural systems can be placed directly on metal supports. Structural systems are generally water tight systems and can be used at low slopes, down to 1/4” in 12”. Architectural systems generally require quick drainage to function and are sloped no less than 2” in 12”.

Galvalume coated steel is the most popular metal for structural applications; steel, painted to complement building design, is the most popular metal for architectural applications. Other metals used for architectural applications include aluminum, zinc and copper.

Ideal application: Buildings where the roof is visible and where roofs are less than 200 feet wide for architectural systems. Buildings where adding some slope is needed, fit structural systems well.

Potential problems: Metal systems generally have a higher first cost than other systems. The amount is dependent on the choice of materials and system. For reroofing, where it is necessary to build some slope, the additional cost for metal may not be much higher.

FOAM

Description: Foam roofs are a combination of an insulating foam that is sprayed-in-place and a protection layer for the foam. The protection layer is commonly a liquid-applied coating placed over the foam. Although the foam itself is a roof, it needs the protection afforded by a coating and/or gravel because the foam is susceptible to damage from ultraviolet (UV) light.

Ideal application: Roofs that are most suited to use spray foam include those that have a slope to drain, are still sound, and/or have unusual configurations. These roofs are manufactured by the operator as the foam is sprayed which allows easy conformance to unusual roof configurations, as well as the ability to smooth transitions and customize slope to drain as needed.

Potential problems: These systems are more susceptible to roof traffic. Birds have been known to be a problem for foam roofs. Possible solutions to combat birds is to use roofing granules in the wet coating as it is being applied or use foam systems known not to have the problem. UV protection must be maintained for the foam to work. If the protection is from a coating, the coating must be patched when damaged.

To determine materials properties, degradation mechanisms, weather effects, and durability testing approaches for single-ply, built-up, and metal roof systems, the research team acquired ASTM special technical publications relating to corrosion, roofing research and standards development, building coatings, accelerated testing techniques, structural health monitoring, and building codes; ROOFER manuals on single-ply and built-up roof systems; and RIEI manuals on single-ply, built-up, and metal roofing systems. As part of a task subcontract, MIT reviewed publications to determine failure modes and mechanisms relating to roofing systems with special emphasis on weathering, snow loading, chemical attack, and freeze-thaw cycling effects. MIT also compiled ASTM standards for testing roofing system components. A preliminary summary report covering these topics has been prepared by MIT with the final report due at the INEEL by September 30, 1998.

Roof Degradation Mechanisms at INEEL

To determine the degradation effects of concern at the INEEL, the research team initially evaluated three classes of degradation effects, weather, human use, and poor facility management. Improper design and installation of a new roof or improper repair of a roof can accelerate degradation of a roofing system.

For example, the trend in recent years at the INEEL has been to replace built-up systems by applying a single-ply system over the built up. If the single ply overlay is not compatible with the built-up roof, degradation may be accelerated. Adding structures on the roof after installation or improper repairs can also lead to roof degradation. Roof system inspectors and designers at the INEEL compiled the following lists of potential degradation mechanisms.

Weather That Degrades Roofing

- Solar radiation
- Temperature cycling
- Wind uplift
- Frost dams on eaves (steep slope roofing only)
- Corrosion (mainly on metal roofs)
- Ponding of water

Human Use That Degrades Roofing

- Foot traffic
- Chemical spills

Facility Practices That Degrade Roofing

- Foot traffic for maintenance purposes
- Tools, equipment dropped on roof surface
- Antennae, guy wires, penetrations etc. added by maintenance people after roof installation
- Poor maintenance or inspections as evidenced by
  - Clogged drains
  - Loss of ballast
  - Debris left on roof surface
  - Lack of, or poor, flashing details
  - Growth of vegetation
  - Lack of careful monitoring of roof access

Designs That Degrade Roofing

- Inadequate provision for movement of various roof components

- Inadequate slope
- Inadequate number of roof drains
- Metal flashing improperly detailed
- Improper roofing membrane for intended application
- Penetrations and roof curbs improperly detailed
- Roof deck inadequately supported
- No roof walkways provided for maintenance purposes or inspection.

Roof Inspection and Maintenance at INEEL

Current roof maintenance management practices address roof system periodic inspections. Budgets determine what percentage of the roof systems, due for inspection, are inspected. INEEL inspectors are not currently involved in the acceptance inspection process for newly installed, repaired, or replaced roof systems.

Roofs of INEEL landlord buildings are inspected every 2 years. Under the ROOFER system, the roof membrane and flashing are visually inspected and assigned a condition index based on previously established ranking criteria. The condition index can range from 100 (perfect) to 0 (failed) based on distress conditions observed by trained inspectors. By treating the membrane and flashing as separate components of the roof system, ROOFER provides a more accurate assessment of component condition, waterproof integrity, and maintenance, repair, and replacement needs. Roof evaluation also considers the condition of the insulation. At INEEL, insulation is inspected using thermography, when appropriate. The insulation condition index is either 100 (no water infiltration) or 0 (water infiltration).

Values calculated by ROOFER for the membrane, flashing, and insulation condition indices are combined to produce a roof condition index, which is an overall condition rating for a roof or roof section. Roof inspections and the reports that ROOFER generates give costs for both repairs and replacement. If needed repairs are made, ROOFER will give repair procedures and added years of roof life over roof life without repairs. The ROOFER data are used at some facility complexes at the INEEL to determine a cost effective, proactive roof maintenance strategy. However, ROOFER provides condition indices only for built-up and single-ply systems, which account for 31% of INEEL roof systems. Table 1 lists the amount of INEEL roofing entered in ROOFER.

Table 1. ROOFER data (single-ply and built-up roof systems) for INEEL.

	1996 ROOFER Data (totals in ROOFER)	1998 ROOFER Data (totals in ROOFER)
Square footage	945,513	1,145,109
Number of buildings	71	92
Number of roof sections	183	210
Thermography (square footage inspected that year)	237,663	125,068

INEEL metal roofs are currently inspected visually, when appropriate, but no roof condition index is generated based on set standards, as ROOFER does not include metal roof systems. This project has made the first step in developing a methodology for standardized inspection of INEEL metal roofs as described below.

Although condition indices are used at some INEEL facilities to determine a cost effective, proactive roof maintenance strategy for single-ply and built-up roofs, INEEL has not defined minimum performance standards for roof systems and thus maintenance criteria vary based on individual facility practices. A standardized, INEEL-wide approach for roof maintenance and life cycle cost estimating would be wise. (A standardized process for making roof system decisions could be much like the current INEEL process for welding practices.)

Because ROOFER does not provide guidance for roof materials selection, a patent record idea was submitted by N.M. Carlson, L.L. Torres, and C.C. O'Brien to include materials properties in a relational database for INEEL roof management. The database would incorporate ROOFER data, National Oceanic and Atmospheric Administration weather data, known degradation mechanisms, INEEL historical roof system management data, manufacturers' recommended roof practices for warranty coverage, and results of durability testing to provide the end user with candidate roof systems most appropriate for INEEL. Although the idea was reviewed favorably by the Manufacturing Intellectual Property Committee, no path to development of the database has been identified at the present time.

Report and Seminar

As part of the research effort a document, *Distresses of Single-Ply Membrane, Built-Up, and Metal Roofs at INEEL*,[4] was prepared following ROOFER format explaining single-ply and bituminous built-up roof distresses and providing photos of INEEL roofs as examples of many of the distress types found at INEEL. The ROOFER format was used as a guide for developing the distress types for metal roof section of the report.

A seminar format was selected as the method, in addition to the report, to effectively relay the information on INEEL roofing system materials, distresses, and management practices to facility and operation personnel. An independent roofing consultant, Kami Farahmandpour, a senior roof system evaluation engineer for Construction Technology Laboratories, Inc of Skokie, IL, conducted the seminar at INEEL on August 31, 1998. Members of the research team meet with the consultant to establish a seminar format. The topics covered in the seminar were understanding roofs, design approaches, evaluation techniques, roof management, recommendations for the INEEL, and deficiencies in INEEL roofs. Research team members provided photographs and details on specific distresses in INEEL single-ply, built-up, and metal roof systems to ensure the audience understood the types of issues faced in implementing a maintenance management model at the INEEL. For single-ply and built-up roofs, each photo caption described the distress; gave distress type and severity; identified the roof material, building, roof section, installation date, and photograph date; and listed contributing factors for the indicated distress. The consultant provided the contributing factors criteria. An explanation and photo example for each contributing factor are provided here.

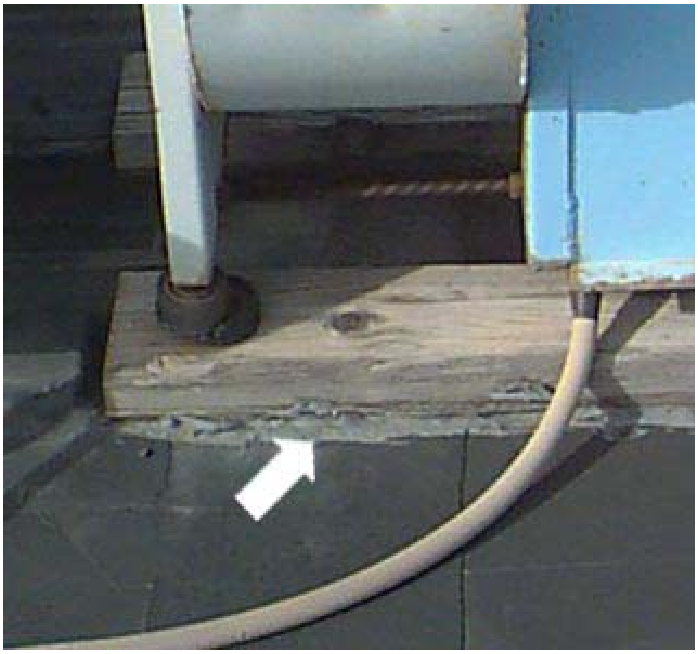
Design: This contributing factor indicates a possible deficiency in the design of the roofing system. Deficiencies in design can include inappropriate detailing of the roofing system or lack of sufficient details and specifications to address the field conditions and requirements for the roofing system. For example, if counterflashings are missing from a roofing system, and the design of the roof did not include requirements for installation of counterflashings, design would be considered a contributing factor to deterioration that is attributed to lack of counterflashing.

Roof Type: BUR—Asphalt, pea gravel
Location: CPP 637, Section D
Installed: Photo: 6/23/98
Contributing Factors: Design

Improper location of drain. Low Severity

Installation: This contributing factor indicates a possible deficiency in the installation of the roofing system or other roof-top equipment. Roofing system or roof-top equipment installation can be considered a contributing factor when installation of one of their components does not meet the design, industry standard, or manufacturer requirements.

Roof Type: EPDM
Location: CF 633, Section A
Installed: 1981 Photo: 6/22/98
Contributing Factors: Installation



Equipment support not sealed at the membrane allowing water to penetrate. High Severity

Materials: This contributing factor indicates a deficiency due to limitation of a material, or normal deterioration. It does not necessarily indicate a deficiency in the material.

Roof Type: EPDM
Location: CF 690, Section B
Installed: 1996 Photo: 6/22/98
Contributing Factors: Maintenance, materials

Stripping material is open. High Severity

Repair: This contributing factor indicates manifestation of a deficiency caused by improper repairs to the roofing system.

Roof Type: EPDM
Location: CF 633, Section C
Installed: 1981 Photo: 6/22/98
Contributing Factors: Repair

Temporary membrane patching different type of material. Medium Severity

Maintenance: This contributing factor indicates manifestation of a deficiency that could be prevented through maintenance of the roofing system and its associated components.

Roof Type: BUR—Asphalt, Smooth;
Aluminum Coating
Location: IF 603, Section M
Installed: 1996 Photo: 6/4/98
Contributing Factors: Maintenance

Cracks extend through one or more plies. High Severity

Freeze/Thaw Testing

To conduct durability testing on candidate roofing systems, the capability to conduct freeze/thaw testing is required. Freeze/thaw cycling is a primary cause of roof degradation at the INEEL. A chamber capable of holding 4 ft × 4 ft roofing sections has been determined to be an appropriate for initial roof testing. The chamber will enhance the INEEL durability testing capabilities and will be used by other projects, both DOE-EM and non DOE-EM related. Chamber procurement is complete with only the installation and personnel training pending.

Software

An assessment of available database software was performed by members of the INEEL software-engineering group to determine applicability of that software for the life-cycle management engineering model. The following recommendations were provided regarding available software:

Access
Platform: 486 or higher
Operating System: Windows 95, Window NT
Cost: $339 (already included in Microsoft Office Professional)
Developer’s Toolkit: $499
Capabilities

- Database capacity—1.2 GB per database (NOAA data currently ~24 MB)
- Wizards for easy development
- Access via ODBC (Open Database Connectivity) drivers to many different data sources

Provides a hyperlink data type to open an Office document or URL address

- Html capabilities for developing Web applications
- Developer can provide an executable so access is not needed on the destination machine

(The installation wizard creates a set of diskettes which would include setup.exe, database files, DLL files, and any other files needed on the destination computer
Advantages

- ROOFER data is currently housed in an Access data
- Highest number of ease of use features of the Microsoft products
- Programming Language is Visual Basic – same as used in other Microsoft Office applications
- Currently the company standard so it is widely available and there is expertise

Visual FoxPro
Platform: 386 or higher
Operating System: Windows 95, Windows NT
Cost: $499
Capabilities

- Database size—2.1 GB per table (NOAA data currently ~24 MB)
- Wizards for easy development
- Access via ODBC (Open Database Connectivity) drivers to many different data sources

Html capabilities for developing Web applications

- Full support for object oriented programming
- Developer can provide an executable so access is not needed on the destination machine

(The installation wizard creates a set of diskettes which would include setup.exe, database files, DLL files, and any other files needed on the destination computer)

- Client/Server Connectivity

Oracle
Platform: Any Intel, Unix, many others
Operating System: Windows NT
Cost: $1500
Limitations

- Due to the high cost of Oracle, this option was not investigated any further.

SqlServer
Platform: 486 or higher
Operating System: Windows NT
Cost: $1399
Limitations

- Due to the Windows NT requirement, this option was not investigated any further.

Based on the evaluation of the available software, Access appears to provide the functionality required to develop the relational database. NOAA data were incorporated into Access with relative ease and the ROOFER data are currently in Access. Further evaluation is required as materials properties and durability data must also be entered in the database. The second year research effort would focus on development of the relational database.

NOAA weather data were acquired from the local NOAA office. These data are "quality assured" to meet DOE-ID standards. The data are for the past five-years for three weather collection stations at the site and for Idaho Falls. The data include year, month, and day of record, maximum temperature (maximum daily 2 meter temperature in °C), minimum temperature (minimum daily 2 meter temperature in °C), wind direction during the maximum wind gust of the day (degree), maximum 15 meter gust speed for hour (m/s), daily precipitation (hundredths of inch), average daily relative humidity (%), daily solar radiation (watt-hr/sq. meter), daily UV (milliwatt-hr/sq. meter), CFA daily snowfall (inches), and CFA daily snow depth (inches). UV data are for CFA only and for only the fifth year. MIT has developed a MatLab program to view the NOAA data as no researchers at MIT were experienced in the use of Access. Use of MatLab provides confirmation that the weather data are useable in a relational database. INEEL software engineering placed the NOAA data in Access for the INEEL research team.

Summary

The need for a research-based engineering model for life-cycle management of roof systems at the INEEL has been established. Materials degradation, durability, and compatibility research is required to develop a robust model for INEEL single-ply, built-up, and metal roof systems. In addition, design, installation, materials, repair, facility use, weather, and maintenance factors have been identified as critical inputs to the model. NOAA and ROOFER data are acquired for input to the model, which initially can be operated from Access. Technical reports and publications relevant to the research effort have been located and are available to the research team. An INEEL/MIT collaborative research effort directed by the INEEL will result in a summary report entitled *Aging and Deterioration of Roofing Systems*. A cyclic freeze/thaw chamber has been obtained for durability testing. As part of the research effort, *Distresses of Single-Ply Membrane, Built-Up, and Metal Roofs at INEEL,*[5] was prepared by the INEEL research team and disseminated to INEEL facility and operations as well as DOE-ID personnel. A seminar entitled *Roof Management at INEEL* was presented to provide an open forum for discussion of enhanced INEEL roof management practices. A patent record idea entitled Roof Management Life Cycle Engineering Model was submitted to LMITCO Technology Transfer Office and reviewed favorably by the Manufacturing Intellectual Property Committee.

References

1. M. Y. Shahin, D. M. Bailey, and D. E. Brotherson, *Membrane and Flashing Conditions Indexes for Built-Up Roofs--Volume II: Inspection and Distress Manual*, USA-CERL Technical Report M-87/13, Vol. II., September 1987.

2. D. M. Bailey et al., *ROOFER: Membrane and Flashing Condition Indexes for Single-Ply Membrane Roofs--Inspection and Distress Manual*, USA-CERL Technical Report FM-93/11, April 1993.

3. “Understanding Roofing Systems,” Rewritten by Ted Michelsen from the Roofing Sourcefile, published in *RIEI Information Letter*, No. 60, The Roofing Industry Educational Institute, Englewood CO, Summer 1998.

4. N. M. Carlson, J. L. Bingham, P. J. Howard, and S. L. Palmer, *Distresses of Single-Ply Membrane, Built-up, and Metal Roofs at INEEL*, INEEL/EXT-98-00683, August 1998.

5. N. M. Carlson, J. L. Bingham, P. J. Howard, and S. L. Palmer, *Distresses of Single-Ply Membrane, Built-up, and Metal Roofs at INEEL*, INEEL/EXT-98-00683, August 1998.

ADAPTIVE SENSORS

K. L. Telschow

Scope and Objectives

Nonlinear optical methods offer an imaging solution to DOE-EM sensing problems. Optics has been chosen as the basic mechanism by which the information to be measured is transferred to the sensor because it is noncontacting, suitable for industrial environments, and has “full-field” imaging capability. In addition to sensing data as images, nonlinear optics can perform mathematical image processing and can perform operations that allow for, or adapt to, data and/or interfering (noise) signals. Such adaptive mechanisms are very important for field use. Phase modulation can be used to record surface profile, deformation, vibration, and ultrasonic motion; it can also be used to record changes in optical wavelength leading to applications such as photoacoustic spectroscopy for material property, surface contamination, and trace gas analysis. This program is researching applications of adaptive sensing to aspects of environmental monitoring. The first year’s results show that the nonlinear optical effect in certain materials, when configured for dynamic holographic sensing, can produce sensors that are *self-adaptive*, *self-processing,* and *highly sensitive,* with *wide area imaging* in *real-time*.

A new method for full-field imaging of specific parameters through this dynamic holographic approach using photorefractive materials was recently developed at the INEEL. This new technology can provide continuous *in situ* measurement and processing of information, intrinsic adaptation to interfering background effects, and real-time output that is directly usable by the operator or in automated feedback and control. This program is designed to develop an understanding of the physics of nonlinear optical sensing mechanisms that correlate with physical environmentally-sensitive parameters so that the new technology can be used in environmental monitoring. A new class of sensors that is compatible with automated and robotic industrial methods will result. In the first year of the program we investigated the physical mechanism leading to the self-adaptive property and laid the groundwork for implementing self-adaptive sensing in a variety of environmental monitoring applications. We will investigate nonlinear optical interferometric feedback and self-oscillation mechanisms for measurement of specific environmental parameters, from spectroscopic chemical identification to the integrity of storage containers, that indicate corrosion or contamination of surfaces.

Technical Accomplishments

Background

The Office of Environmental Management must characterize, treat, and dispose of hazardous and radioactive wastes that have been accumulating at sites throughout the nation. Sensing is an important part of this effort in that before, during, and after remediation, information on the physical and chemical state of the materials must be known. Some of the EM sensing issues that must be addressed are:

- Determination of the physical state of hazardous waste in storage tanks. This waste includes organic and inorganic chemical compounds in solid, colloidal, slurry, and liquid phases.
- Determination of the structural and physical integrity of storage tanks (e.g., leaks, fracture and fatigue damage, corrosion).
- Determination of the physical and microstructural properties of aged fissile materials.

- Characterization of mixed hazardous and low-level radioactive waste stored in drums and boxes and of incoming waste streams.

- Effluent monitoring to optimize treatment operations and to ensure compliance with environmental requirements.

- Real time monitoring of waste streams and effluents for heavy metals, toxic metals, dioxins, and volatile organic compounds.

- Determination of the hydrodynamics of fluids in cracked media, transport phenomena and phase separation at surfaces, and radiation-enhanced dissolution at interfaces to provide a better understanding of waste form leaching.

Many of these sensing problems can be solved with acoustic, ultrasonic, or optical nondestructive evaluation (NDE) methods or optical spectroscopy. However, *in situ* monitoring requires that the measurements be noncontacting, nonintrusive, capable of covering a wide area, and compatible with field situations. In addition, the sensor must provide high sensitivity and selectivity for the particular parameter being measured. Successful field implementation requires that the sensor adapt to, or automatically account for, difficulties such as sample or sensor motion, high temperatures, and optical or acoustic radiation fields. Furthermore, intrinsic data processing is required when the need for fast corrective action precludes extensive data acquisition and analysis by remote computers. Optical sensors are ideal for noncontacting measurements; however, they tend to be sensitive to external noise. This project is investigating the use of nonlinear optics as a new sensing methodology for EM sensing problems.

FY-98 Technical Accomplishments

There are four tasks in this project, Self-Adaptive Process Modeling, New Sensor Materials Development, Environmental Sensing Possibilities With Photorefractive Materials, and Interferometric And Holographic Imaging Development. The accomplishments in each of these areas are discussed next.

Self-Adaptive Process Modeling. The basic concept for this sensing project relies on the ability of nonlinear optical interactions in certain materials to process images and automatically adapt to specific outside interferences. When two optical beams interact inside a photorefractive material (PM), the resulting interference distribution of optical intensity produces a spatially modulated pattern of excited charge carriers (either electrons or holes). Excited carriers transport throughout the material, governed by diffusion and drift caused by internally-generated or externally-applied electric fields. After a time that is characteristic of the material conductivity and conduction mechanism, the carrier distribution changes and settles into a new configuration that locally generates a space charge electric field that can be very high. The new space charge electric field distribution produces an “optical grating” that can diffract light through the electro-optic effect. Two-beam diffraction gratings of this type can perform a variety of optical processing functions, such as beam deflection, beam amplification (transfer of energy from one beam into another), phase demodulation, and cross-correlation.

While the basic theory of the photorefractive process is known, use of this phenomenon for adaptive sensing of environmental parameters requires application-specific research to establish detection methodology, detection limits, operating parameters, and material properties for optimum sensitivity. This project is initially focusing on the ability of the photorefractivity process to demodulate phase information placed onto a signal light beam in an adaptive and imaging manner. The first application of this process was to detect very small motions (typically, nanometers or less) of materials caused by standing and traveling ultrasonic waves. (A new “Imaging Ultrasound Camera” resulted from this work and is being patented by the INEEL.) Measurements of ultrasonic motion are an important, calibrated, method for investigating the physical mechanisms responsible for the imaging photorefractive process. Through these studies, we can demonstrate the utility of this sensing approach and learn how it can be most effectively used in environmental monitoring.

Point Measurements of Ultrasonic Traveling Waves—A method was investigated that directly measures vibration amplitude and phase in a metal plate by measuring the photorefractive grating produced at a fixed beat frequency between phase-modulated signal and reference beams. Vibration amplitude and phase allow determination of the ultrasonic mode wavelength and, from this, information about the physical condition and microstructure of the plate. This method accommodates rough surfaces, exhibits a flat frequency response from Hz to GHz, and can be used for detecting both standing and traveling waves. NDE of complex parts often uses ultrasonic wave motion in the traveling wave sense. Our work has shown that the methods being developed on this project can be used for both resonant (standing wave) and nonresonant (traveling) wave measurements. This allows the technique to be used in most applications where ultrasonic methods are used for NDE today, with the significant advantage that the results of the measurement are automatically produced in a an image format.

The experimental setup for point detection of traveling waves is shown in Figure 1. The laser beam is split into two legs, the signal and reference beams. The signal beam reflects off a nickel plate driven continuously at its center by a piezoelectric transducer. Flexural waves travel radially outward from the center of the plate. The traveling wave displacement at the plate surface modulates the phase of the signal beam. The signal and reference beams interact inside a bismuth silicon oxide (BSO) photorefractive crystal. At the output of the crystal, the diffracted wavefront is recorded by a photodetector for the point measurement displacement amplitude and phase while a charge coupled device (CCD) camera is used for imaging. A narrow beam, about 2 mm in diameter, is used for making point measurements and then expanded to roughly 50-mm in diameter for imaging.

Single point measurements were performed by scanning a signal beam across the plate surface along a radius from the excitation point. The amplitude and phase results were recorded to show a frozen-in-time picture of the wave motion, see Figure 2. Elastic theory for plate waves then allows the wavelength to be predicted based on the material’s elastic constants. Figure 3 shows the good agreement achieved between the measured and predicted wavelengths over a large frequency range.

Imaging Measurements—The point method described above was extended to image the ultrasonic motion over a large surface area of the plate. This capability for imaging, because the detection mechanism is holographic, is a significant feature of the photorefractive measurement technique that offers advantages for implementation in a field environment. The distributed character of the photorefractive holographic process creates a grating distribution that corresponds to the phase modulation at all points on the specimen surface simultaneously. The output beam intensity can then be measured by an array of detectors, or even a highly pixelated device such as a CCD camera. Figure 4 shows images obtained of the traveling wave modes of the nickel plate. The flexural mode wavefronts traveling outward from the center are clearly defined, and the relative phase of the displacements is readily distinguishable. For qualitative inspection, the eye integrates over multiple video frames. This makes it possible to easily detect subtle patterns that might not be as easily extracted by digital image processing methods. Also, the entire pattern can be made to change its phase continuously, perhaps at about 2 Hz, so that the appearance is that of waves emanating from the center and traveling outward. This is physically equivalent to the actual traveling wave motion except that the observed wave is much slower than, and independent of, the actual wave frequency. The photorefractive process yields a true picture of the actual wave vertical displacement motion and does not require any additional processing to generate the images of Figure 4.

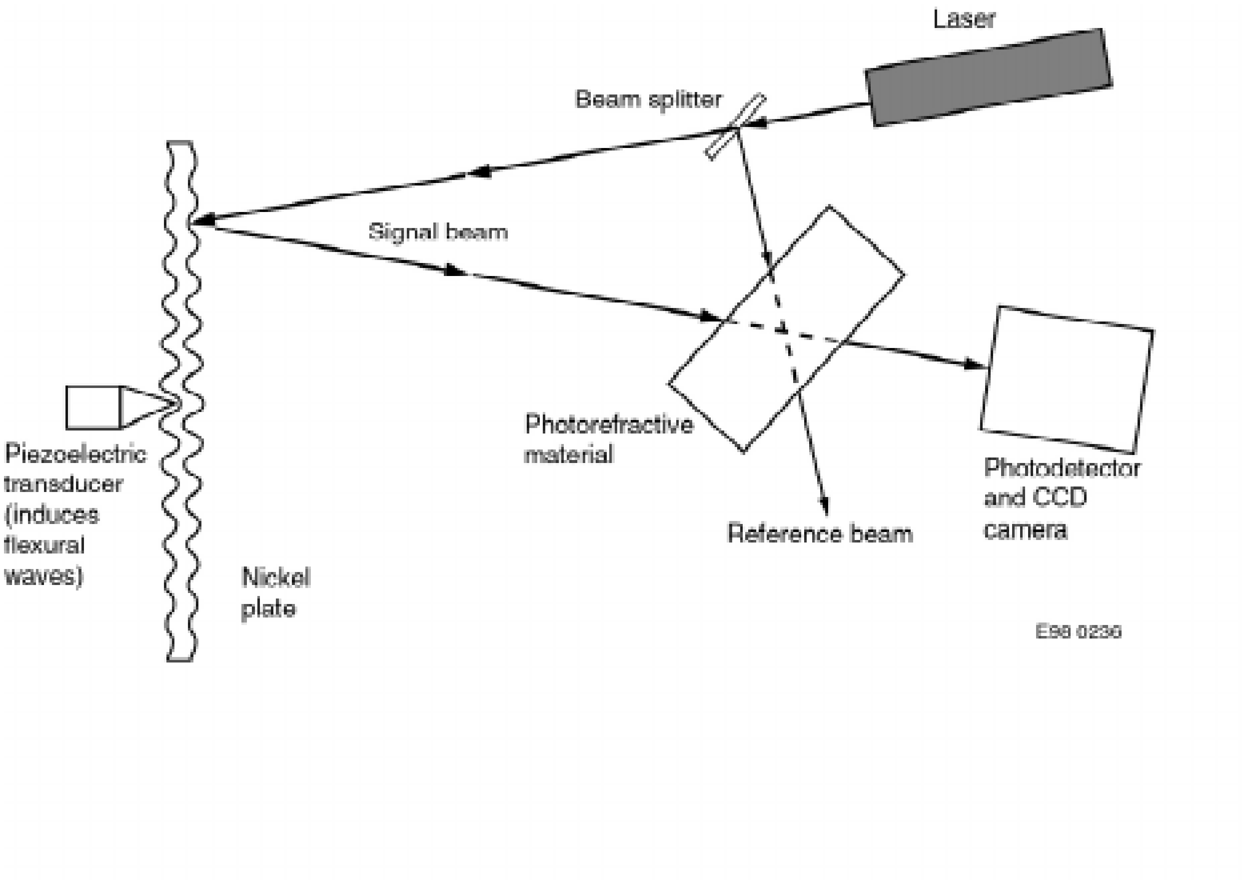


Figure 1. Basic experimental setup for photorefractive demodulation of optical phase.

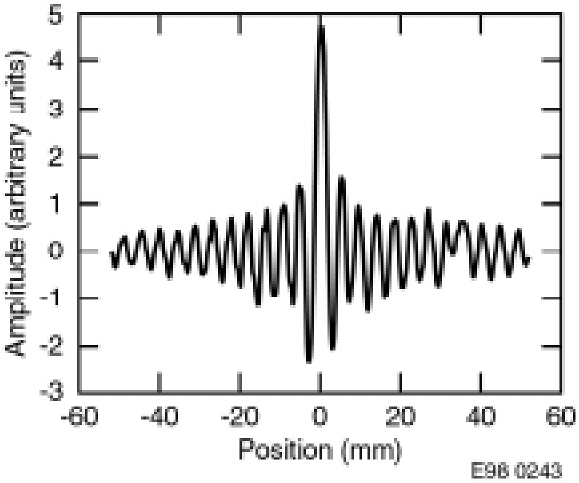


Figure 2. Traveling wave displacement amplitude in a 0.13 mm thick nickel plate.

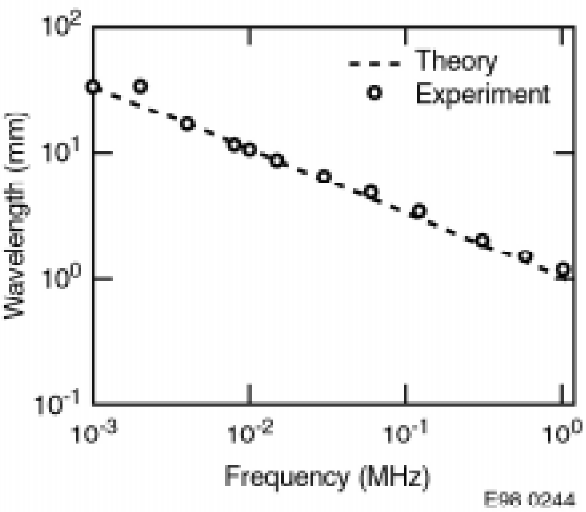


Figure 3. Measured vs. predicted wavelength as a function of frequency for the nickel plate.

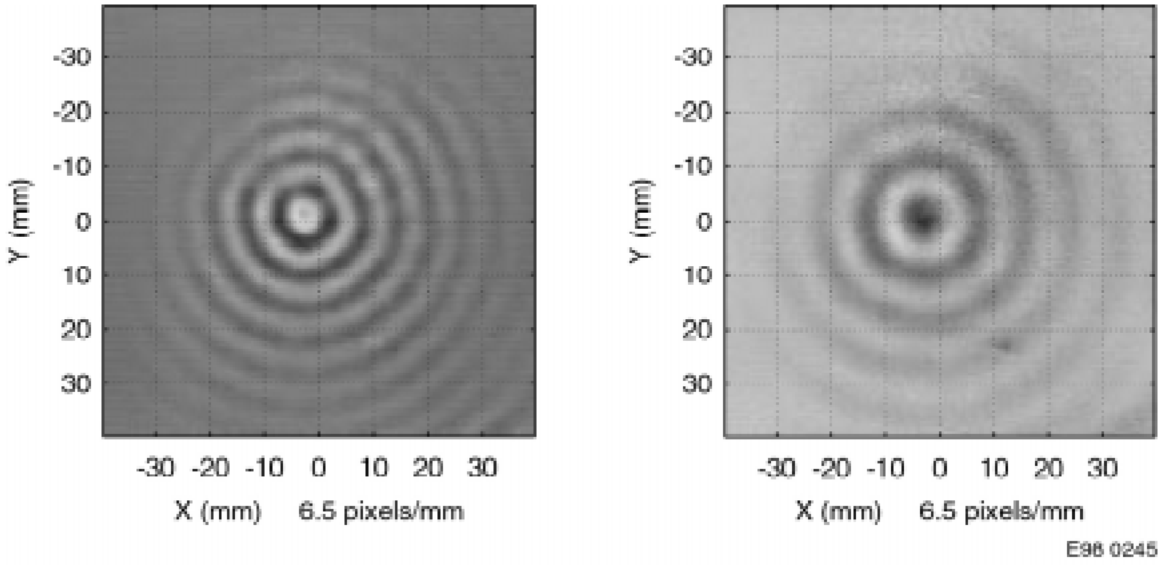


Figure 4. Images of traveling Lamb waves in nickel at 15 kHz (left) and 30 kHz (right). The background has been subtracted.

If the specimen is elastically anisotropic, then the wave speed varies with the propagation direction. Figure 5 shows this type of behavior for traveling waves in a sheet of carbon fiber composite. The highly oblong wavefront pattern seen in Figure 5 shows the anisotropy clearly and immediately. The right frame shows the wavelengths measured for this composite sheet in the directions along and perpendicular to the fibers as a function of frequency. A great deal of information about the anisotropic elastic properties of the sheet can be obtained directly from this image.

Anisotropic Self Diffraction in GaAs—Many photorefractive materials, such as BSO and gallium arsenide (GaAs), are anisotropic. For these materials, the two-wave mixing process depends on optical beam polarizations and propagation direction with respect to the crystalline axis. This year, with the help of summer student Jon Holland, two-wave coupling in GaAs was modeled, taking into account the signal and reference beam polarizations and crossing angle with regard to the GaAs crystalline axis

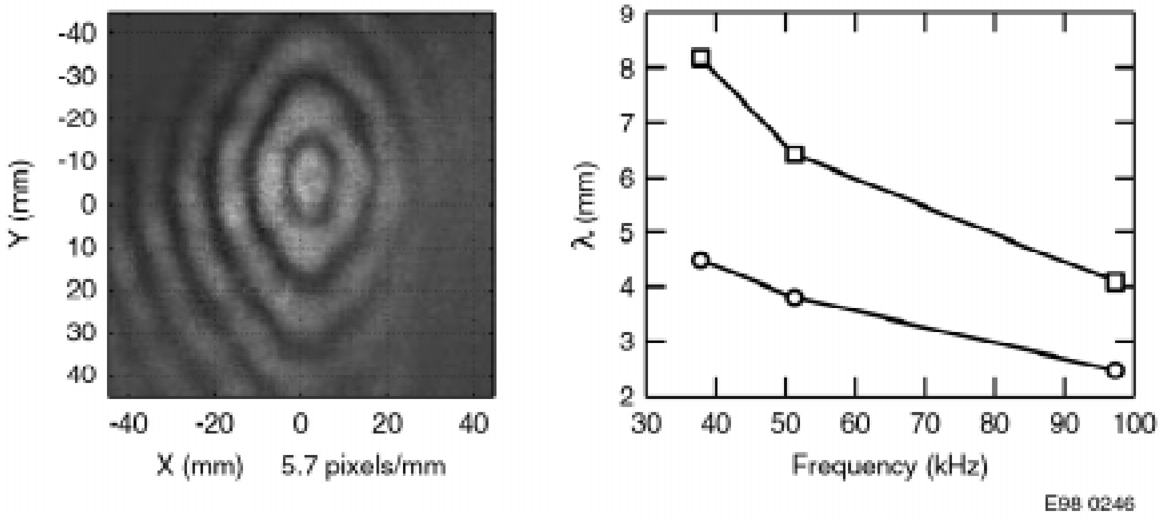


Figure 5. Traveling wave at 37.8 kHz in a 0.178 mm thick, anisotropic, carbon fiber composite sheet with an isotropic resin matrix. The fibers are parallel with the vertical direction. Measurements of the wavelength in the vertical (x) and horizontal (o) directions are shown to the right.

orientation. Two-wave mixing in GaAs was also measured for a variety of orientations and polarizations. Very good agreement was found between the measurements and the calculations for most the orientations studied. Discrepancies based on anisotropic attenuation were found that altered the results by as much as 10 to 15% for some orientations. Figure 6 shows the agreement obtained for the orientation yielding the largest two-wave mixing gain.

This work has given us confidence that the photorefractive mixing process is correctly being described in these anisotropic materials for the time independent DC case. Most of the measurement methodologies being investigated on this project involved alternating or AC phase modulations that must be demodulated by the two-wave mixing process. The DC case will be extended to account for AC modulations in FY-99.

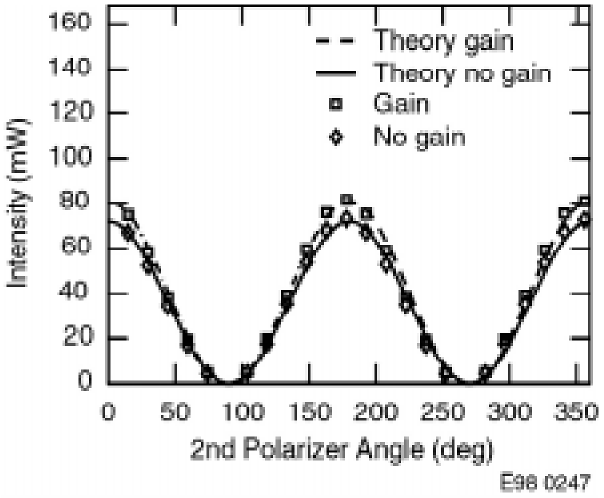


Figure 6. Calculated and measured two-wave mixing gain of GaAs for the orientation yielding the largest gain.

Modeling Conclusions—The photorefractive optical two-wave mixing process has been studied theoretically and experimentally, resulting in better understanding of the process and its limitations. The process was used to measure the ultrasonic motion on solid material surfaces and was shown to have a detection sensitivity of 5×10^{-6} nm(watt/Hz)$^{1/2}$, which corresponds to a phase detection sensitivity of about 4×10^{-6} radians; this is about a factor of 75 greater than the theoretical limit of 3×10^{-8} radians. To date, the limitations are electronic and laser phase noise and photorefractive sensitivity, all of which can be reduced. The work on ultrasonic wave imaging has shown the great utility of this approach—the imaging output is suitable for direct viewing or recording with a CCD camera. In addition, the method is capable of flat frequency response over a wide range (Hz to GHz) and is applicable to rough surfaces.

New Sensor Materials Development. The optically nonlinear material is the heart of the photorefractive measurement process. The sensitivity, speed of response, and optical wavelength of an adaptive system all depend on intrinsic properties of the photorefractive material. The availability and cost of this material will also greatly affect the availability and cost of the measurement system. This project is searching for new and better materials, particularly ones with high gains and fast response speed. The high gain is needed to allow the use of lower cost, less powerful, lasers than those currently being used in laboratory research and the faster response speed is needed to better select against acoustic and vibration noise in field applications. Two collaborations have been explored during FY-98 with researchers at universities to find better materials. These collaborations involve organic and inorganic materials.

Organic Polymer Materials—A subcontract to support research and a graduate student has been established with Professor W.E. Moerner of the University of California at San Diego (UCSD) (soon to be at Stanford University) to explore the use of organic polymer materials. These materials have been shown to provide very high two-wave mixing gains that result in nearly 100% diffraction efficiency, but their response speed is relatively slow compared to the inorganic crystalline materials now being used. Optically active polymers show considerable promise due to ease of fabrication, low cost, and more options for customization than traditional inorganic photorefractive crystals. Prof. Moerner and his colleagues have developed a polymer material that has response speeds approaching that of GaAs, the fastest material being studied at present. Samples of this material have been sent to the INEEL and are currently under study. Professor Moerner presented a seminar at INEEL entitled “Physics and Chemistry of High-Performance Photorefractive Polymers” in August.

Inorganic Semiconductor Materials—Semiconductor photoelastic materials that alter their local optical properties in response to light can also be used for dynamic sensing. These materials have diffraction efficiencies near 100%. They are primarily active in the infrared region of the spectrum, which makes them less hazardous to eyes. Another advantage of these materials is their sensitivity, which has the potential to reduce the amount of light required for detection, and hence the size, cost, and complexity of the imaging sensor system. This project, in conjunction with Laboratory Directed Research and Development work, is pursuing collaboration with Professor K. Lynn, Director of the Materials Science Institute at Washington State University, to investigate the ability of certain semiconductor materials to form gratings for sensing. An informal collaboration is in place in which INEEL will test certain materials produced by Professor Lynn. Another potential partner that fabricates semiconductor crystals is the Johnson Mathey Co.

Environmental Sensing Possibilities With Photorefractive Materials. The first environmental sensing application under study is detection of pollutants in the atmosphere, and adsorbed onto surfaces, using photoacoustic spectroscopy. The goal of this work is to use the dynamic holographic imaging method to develop a directly imaging form of photoacoustic spectroscopy.

Figure 7 shows some of the many interactions between absorbed modulated light and materials. The absorbed light produces an alternating modulation in the surface displacement, surface temperature, and overlying gas temperature and density, in addition to launching elastic waves in the material and acoustic waves in the gas. All of these processes will produce a corresponding modulation in the phase of a probe light beam reflected off the surface of the material. It is this small phase shift that dynamic holography detects. Previous work has shown that dynamic holography can image ultrasonic motion. This work is being extended to produce an imaging form of photoacoustic spectroscopy that could potentially be used for field imaging of pollutants in the atmosphere.

Photoacoustic heating of gas from the atmosphere modulates the index of refraction for the optical probe beam either along its path or at the adsorption surface. Interferometric techniques can detect and demodulate this phase shift. It has been estimated mathematically that the net temperature change that can be measured along a 1 cm probe beam path can be as small as 34 micro-degrees at atmospheric pressure and room temperature. Clearly, the interferometric phase detection method is extremely sensitive. Photoacoustic spectroscopy in gases has been performed by others, who have demonstrated detectabilities for certain chemical compounds at the part-per-billion (ppb) level. Table 1 shows and references some of these results and the particular chemical compound detected. Our research will add the ease of operation due to the adaptive nature of the photorefractive process as well as its intrinsic imaging capability to these types of measurement.

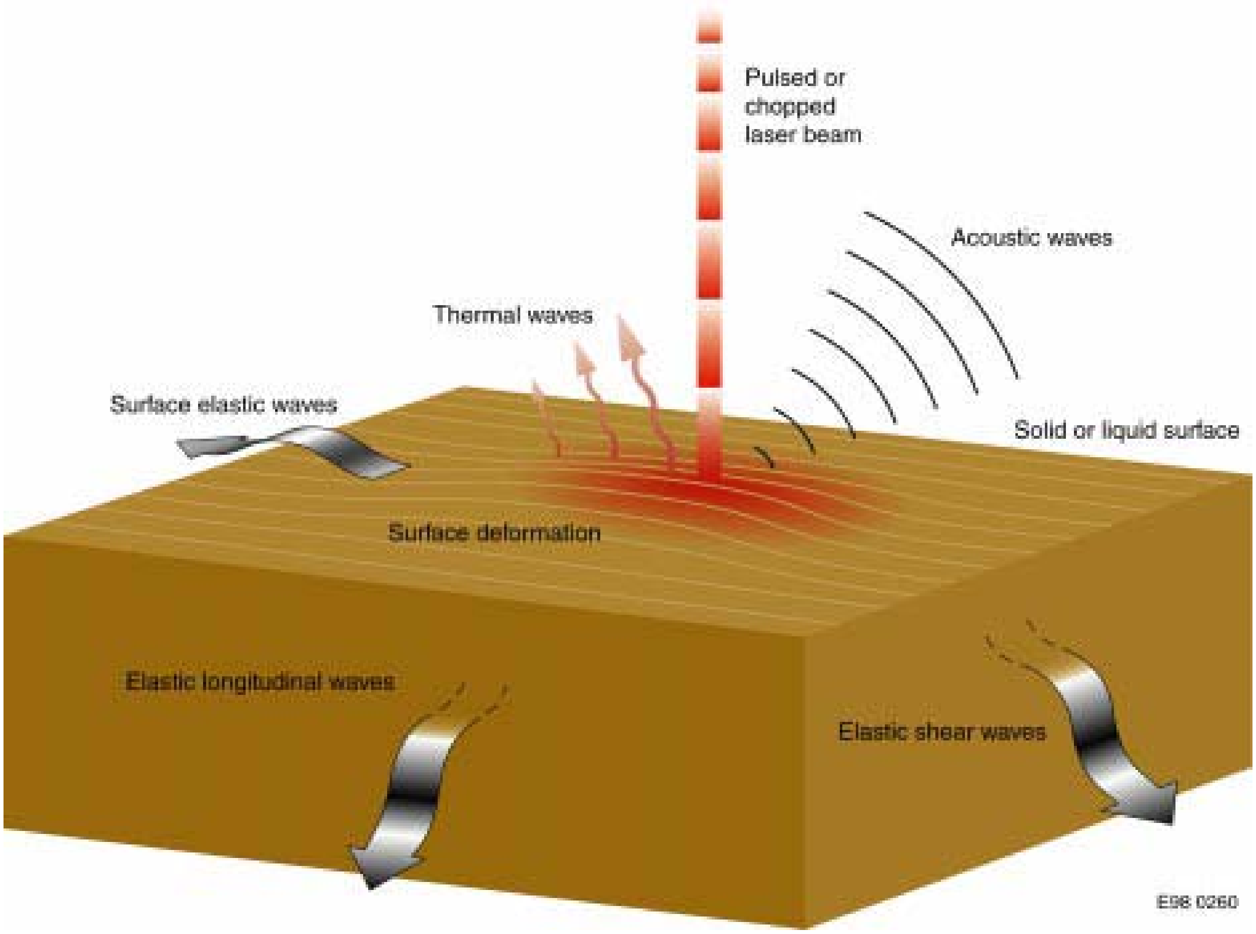


Figure 7. Possible modulated light/material interactions.

Table 1. Detectability limits for various compounds found by other researchers using phase detection photoacoustic spectroscopy similar to that proposed on this project.

Investigator	Cell Length (cm)	Analyte	Matrix	Detectability
Davis et al., Appl. Phys. Lett. 36,515 (1980)	10	CH_3OH	Air	40 ppb
Weston et al., Appl.Opt. 32, 828 (1993)	10	SF_6	Air	16 ppb
Lin et al., Appl. Opt. 24, 422 (1985)	20	C_2H_4	N_2	300 ppt
Campillo et al., Opt. Lett. 5,424 (1980)	15	NH_3	Air	5 ppb
Mazzoni et al., Appl. Opt. 30, 758 (1984)	1	N_2H_4	N_2	30 ppb

Interferometric And Holographic Imaging Development. Many detection schemes involve intermittent or continuous monitoring of some physical factor at a single location. This project is developing the ability to perform full field imaging, that is, to make simultaneous measurements at many locations and produce an image of the spatial distribution of the factor over an extended area at a given time. Such images are the ideal way to present data for human interpretation, and this type of image has been extensively used for satellite and aerial multi-sensor spectral data. This project is extending full-field imaging to other areas of environmental sensing. INEEL has shown that important measurement parameters can be output directly on television screens in a manner that provides wide areal spatial distribution and allows simple interpretation. At present, the sensitivity of full-field imaging is a 1000 times lower than that of point measurements. New techniques are needed to close this gap. We are addressing this problem through unique new approaches and collaborations with microelectronic photometric camera developers and institutions.

Much of this year’s effort has been devoted to extensive improvements to the imaging processing and the data acquisition and analysis techniques with the help of summer student Dallin Anderson. The imaging setup is shown in Figure 8. An SMD model 1M15 digital camera was purchased. It is the state-of-the-art in fast, single channel, digital cameras; it has 12 bits range and 1,000 × 1,000 pixels and is capable of operating at 15 fps with 1,000 × 1,000 pixels and at 30 fps for 512 × 512 pixels (2 × 2 binning mode). This camera substantially improved the quality of our data, as well as allowing much better control over camera functions such as synchronization. To improve control over the camera and to implement a background subtraction scheme, a new custom electronics package was designed, built, and placed into operation. An automatic background removal process was developed that greatly improved the quality of the data by removing most of the fixed pattern noise (DC component).

Other accomplishments this year involved new photorefractive materials for sensing the data. Most of the prototype development has been with BSO, but it has a rather slow response time (30 ms). Faster materials would be less sensitive to vibrational noise. Preliminary tests on one faster material, GaAs (response time of about 1 ms), have shown that it can be used in an imaging mode with considerable improvement in response time and low frequency noise rejection. This material operates in the near infrared. A high power, long coherence length, IR laser operating at 1.064 μm was acquired for imaging with GaAs. This new system will be in operation early in FY-99. Also, the new photorefractive material, based on optically active polymers, received from Prof. Moerner will be tested for imaging capability in FY-99 when brighter coherent laser sources at ~650 nm become available. Efforts have been made to acquire a new class of inorganic semiconductor photoactive crystals that provide good sensitivity and response time; they will be tested as they become available. The sensitivity of these materials has the potential to reduce the amount of light required for detection, and hence the size, cost, and complexity of the imaging sensor system.

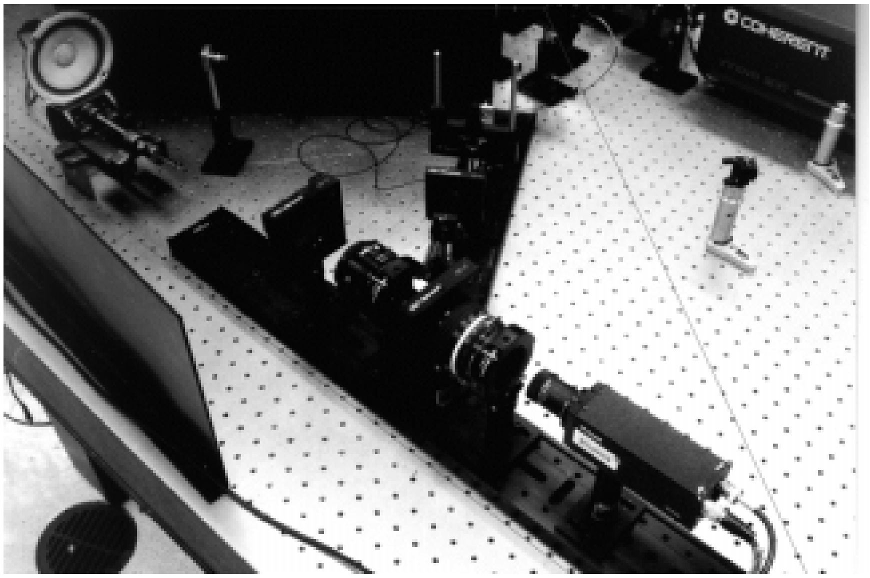


Figure 8. Picture of the imaging setup showing the two-wave mixing region near the center, sample to the left and the CCD camera on the right.

The advantages of direct imaging provided by this methodology have been demonstrated experimentally and progress has been made toward achieving high sensitivity at every pixel concurrently with direct imaging. New capability has been acquired through capital equipment purchases. Development of a system for the first environmental sensing application, photoacoustic spectroscopy for detecting pollutants in the atmosphere or adsorbed on surfaces, has begun. Theoretical modeling determined detection limitations and direct measurements will begin in FY-99. Work is underway to extend this imaging measurement methodology to other sensing needs in the environmental community.

FY-98 Publications and Presentations

K. L. Telschow and V. A. Deason, " Structural Vibration Mode Imaging Using Photorefractive Holography," *Proceedings of the 16th International Congress on Acoustics / 135th Acoustical Society of America Meeting*, Seattle, WA, June 20-26, 1998, pp. 1873-1874.

K. L. Telschow, V. A. Deason, R. S. Schley and S. M. Watson, "Imaging of Lamb Waves in Plates for Quantitative Determination of Anisotropy using Photorefractive Dynamic Holography," submitted to *Review of Progress in Quantitative NDE,* Vol. 19, edited by D. O. Thompson and D. E. Chimenti (Plenum Press, New York, 1998).

Summary

The photorefractive dynamic holographic process has been successfully modeled theoretically and demonstrated experimentally, even for anisotropic materials, and the limits of detection have been determined through measurements of ultrasonic motion in materials. The advantages of direct imaging provided by this methodology have been demonstrated experimentally and progress has been made toward achieving the ultimate in sensitivity at every pixel concurrently with direct imaging. New capability has been acquired through capital equipment purchases. Collaborations between INEEL and university researchers have been established for the development of enhanced materials for the detection and imaging processes. Development of a system for the first environmental sensing application, photoacoustic spectroscopy to detect pollutants in the atmosphere or adsorbed on surfaces, began.

Theoretical modeling determined detection limitations; measurements will begin in FY-99. Discussions are underway to extend this imaging measurement methodology to other sensing needs in the environmental community.

INTEGRATED SENSORS FOR IN SITU CHEMICAL MEASUREMENT

P. Castle

Scope and Objectives

The Integrated Instrumentation for In Situ Chemical Measurements (I^3SCM) research task within the Core Capabilities and Technical Enhancement Program (CCTEP) has an overall goal of carrying out research that will provide the basis for new instrumentation or methods by which environmental chemical measurements can be made. One of the principal objectives for the program is creation of instrument concepts that allow for the development of smaller instruments that are easier and/or less costly to take into the field. There are also opportunities for instrumentation with these properties to have an impact in the area of process monitoring.

The range of detection methods being employed in this research includes optical measurements, ion current measurement, and surface acoustic waves. Several means are being explored to enhance the sensitivity and selectivity of these detection methods. These include membrane separation for microsamplers and sample conditioning as well as fluorescence tagging with analyte specific biological species.

For FY 1998 there were five primary divisions of the I^3SCM research program:

1. Membrane Characterization by Mass Spectrometry
2. Microlasers
3. Biosensors
4. Ion Mobility Spectrometry
5. Microinstrumentation

Technical Accomplishments

Background

Membrane Characterization by Mass Spectrometry. Detecting organic compounds at trace levels, especially in aqueous media, is considerably important in many fields, e.g., environmental, medical, and process applications. Many techniques are available for this. Performance of each technique can be enhanced by configurations that exclude unwanted (corrosive, interfering, diluents) chemicals. Due to its specificity, mass spectroscopy is one of the most useful techniques. The value of combining a membrane and mass spectroscopy has been recognized and is actively being developed. It has been given the name membrane introduction mass spectrometry (MIMS). The primary strength of MIMS is its ability to allow 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, depending on the membrane chosen. Some polymers have shown enrichment factors of over 8,000 for certain organic compounds. However, many other compounds currently show little, if any, enrichment with the present polymer types.

“Depending on the membrane chosen”—is the key phrase. The objective of this project is to develop membranes that will enhance the applicability of MIMS to environmental applications and lead to improved sensor materials. An INEEL-developed set of analyte-specific MIMS membranes could have a significant impact on environmental related sensing, monitoring, and cleanup. The work will synergistically connect two of the INEEL’s core capabilities—separations and mass spectrometry.

The goal will be to provide a series of polymers that will enhance analytical techniques for environmental sensing and monitoring of waste streams and remediation sites. The new systems will be fast, relatively inexpensive, and easily adapted to operation in harsh on-site environments. Even though the method would impact environmental sensing activities directly, there are many other uses for such capabilities, such as in industrial process control and medical diagnostic testing. So the overall impact and the benefits to DOE-EM and LMITCO could come in many forms—direct financial licensing payments, improved production, public relations for helping develop techniques that solve a broad range of cleanup activities, and improved scientific credibility from publishing papers that contribute to the use and understanding of selected polymers in MIMS and other analytical systems.

The overall long range goals of the project were divided into four components: (1) Test existing polymers, (2) Design and test polymers with structures to improve performance, (3) Correlate structure and function (build a data base), and (4) Configure a mass spectrometer to operate in the MIMS mode. This work will: (1) develop a new core capability for the INEEL, (2) characterize existing materials as potential sensors for EM and other applications, and (3) give insight into the types of materials that should be produced for further optimization of flux and selectivities for the different applications of interest.

Microlasers. The objective of this task is to develop a compact, time-resolved fluorimeter for the in situ monitoring of bioprocesses, and in particular, the monitoring of biodegradation of subsurface contaminant plumes. The fluorimeter is designed around a new, small-scale laser technology, called “microchip lasers.” The specific goals of the effort are to integrate this device with nutrient-diffusing devices designed to probe particular degradation pathways in the downhole environment.

Fluorescence spectroscopy is a very powerful analytical technique. The determination of parameters associated with the emitted light, i.e., spectral intensity, polarization, and lifetime, provides insight into the structure of substances and how they react with their surroundings. In most real world applications, fluorescence will arise from several emitting species. In these cases, steady-state measurements will provide information only on the average value of the emission, and in general, will not be able to determine the quantity and quality of the emitting species. This is particularly true of biological species with weak, overlapping absorption and emission spectra. In most applications of interest these species are also present with a chemical medium (natural or manmade) that also emits a background signal. Even in cases where fluorogenic enzyme reactions are used to enhance the detection of enzyme molecules or enzyme-linked antibodies, measurement sensitivity can be limited by stray light or background fluorescence from solvents or other reaction products.

Time-resolved fluorescence has been successfully used to analyze complex mixtures, including biological systems. The widespread use of this technology has been limited by the cost and complexity of the instrumentation needed to produce subnanosecond time resolutions. A class of small, robust, solid-state laser devices is becoming available that could aid in transferring the use of this technique into field and process applications. These devices, called microchip lasers, consist of a more-or-less common infrared diode laser that pumps a series of small crystals, producing high repetition rate, high peak power pulses in the ultraviolet to visible regions of the electromagnetic spectrum. The peak powers produced are comparable to large (several hundred pound, table size) Q-switched lasers, in a device that can fit into a package the size of a standard diode.

The MIT Lincoln Laboratory has developed a fiberoptic-coupled, microchip laser. The laser is a passive Q-switch design that does not require any switching electronics, reducing the system size and complexity. In this particular laser, approximately 1 W of 0.8 micron radiation from a standard laser diode is transmitted through an optical fiber to a series of optical crystals (ND:YAG, KTP, and BBO) which may be located at a large (km) distance from the diode pump. The pumping of the Nd:YAG crystal results in the generation of 1064 radiation that is frequency-doubled to visible radiation at 532 nanometers in the KTP crystal and finally quadrupled in the BBO crystal to produce 2 kW (peak power) of ultraviolet radiation at 266 nanometers with pulse widths of the order of 10s of picoseconds in a package that is the size of a pencil. See Figure 1.

The coupling of microlasers and time-resolved fluorescence detectors with nutrient-diffusing devices can provide an effective tool for monitoring biodegradative microorganisms *in situ*. Nutrient-diffusing devices (NDDs) are vessels that release nutrients for growth of microorganisms in and around the device. Incubation of the devices in groundwater via boreholes leads to multiplication of bacteria under natural growth conditions, including temperature, pH, etc. NDDs can be used to detect bacteria, to determine which nutrient amendments stimulate growth, and to determine if inducible biodegradative enzymes are expressed under natural conditions. Growth can be monitored by detecting fluorescent molecules naturally produced by the bacteria. Since these molecules (e.g., aromatic amino acids) are found in all bacteria, highly selective growth conditions are needed to ensure that the fluorescence signal is derived from the bacteria of interest. Such conditions can be achieved by using selective chemical inhibitors in conjunction with selective growth substrates. The excitation/emission spectra for these compounds has been characterized in the literature and are summarized in Table 1. It should be noted that a microlaser could be designed for exciting each of these types of compounds using frequency doubled or quadrupled radiation from various types of neodymium (Nd) lasers.

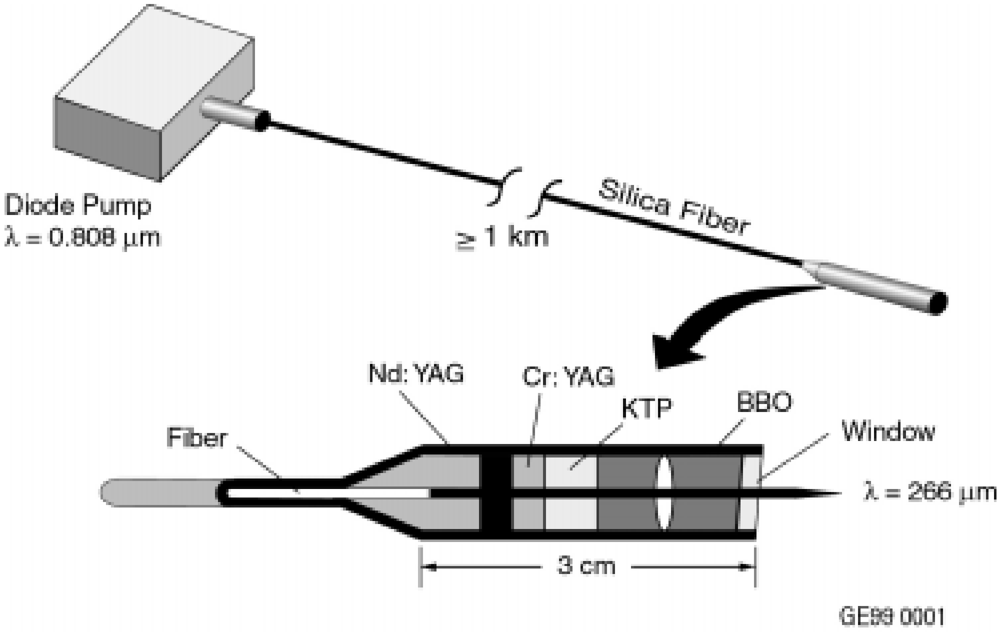


Figure 1. Schematic of a fiber-coupled microlaser for producing 266 nm output.

Table 1. Intrinsic fluorescence in biological molecules.

Compound	Peak Excitation	Peak Emission	Lifetime	Laser
Amino Acids	280 nm	350 nm	1–6 ns	Nd:YAG
NADH/NADPH	340 nm	450 nm	0.4 ns	Nd:YLF
Flavins	450 nm	520 nm	2–4 ns	Nd:YVO_4

Alternatively, fluorogenic substrate probes may be included in the devices; transformation of the probe by the bacterial enzymatic activity of interest results in the accumulation of fluorescent products.

Toluene and trichloroethylene are common environmental pollutants. A variety of bacteria can cometabolically degrade trichloroethylene via oxygenase-catalyzed reactions, including bacteria that use toluene as a natural growth substrate. Several pathways for toluene degradation are expressed in bacteria and are initiated by oxygenase-catalyzed reactions. *Burkholderia cepacia* G4, *Burkholderia pickettii* PKO1, *Pseudomonas mendocina* KR1, and *Pseudomonas putida* mt-2 produce oxygenases that hydroxylate toluene at the *ortho*, *meta*, *para*, and methyl positions, respectively. Toluene 2,3-dioxygenase of *P. putida* F1 oxidizes toluene to *cis*-toluene dihydrodiol. Only strain mt-2 does not degrade trichloroethylene. All of these bacteria use inducible enzyme systems for growth on toluene that are not expressed when the bacteria are grown on other carbon sources (e.g., succinate).

Specific objectives of this project for FY-98 included: (1) developing chemical inhibitors that are highly selective for specific toluene-degradative pathways, (2) initiating and fostering collaborations for the purpose of developing fluorogenic probes that act as substrates for specific bacterial enzymes known to degrade trichloroethylene, (3) developing additional monitoring strategies for toluene-degrading bacteria and (4) procuring, integrating, and testing a benchscale, time-resolved, fluorescence system with subnanosecond resolution. Proposed FY-99 objectives include studies with NDDs containing the inhibitors and probes.

Biosensors. This project was initiated in midyear FY-98 to develop a simple array of biosensors and appropriate detection hardware to demonstrate INEEL capability to produce microsensors. The biosensor components identified for this simple but operational demonstration array include two whole cell sensors responsive to the heavy metal, arsenic, and an antibody to a common organic contaminant, toluene. The arsenic biosensors exploit response, or “reporter gene” mechanisms, including the biological light production, or bioluminescence system (lux) from the marine bacterium, Vibrio fisheri, and the green fluorescent protein (GFP) of the marine jellyfish, Aequorea victoria. Both reporter systems are commonly used to monitor gene expression in living organisms, as well as in vitro. Two parallel whole cell biosensors are being constructed with these systems, in order to assess whether a fluorescent signal resulting from GFP expression is more sensitive than photon detection from the lux system. The immobilized antibody to be used in the array will allow us to examine issues concerning immobilization, stabilization, and utilization of antibodies to detect contaminants in a planar configuration with other types of biosensors adjacent to the antibodies.

Bioluminescent Sensor Concepts—Bioluminescence is widely distributed in the living world, and it has been studied for hundreds of years (for example, Boyle reported on the requirement for air in the emission of light by fungi and bacteria-degrading rotting wood and fish). Organisms ranging from bacteria to fireflies and beetles are known to emit light, with that light varying in its emission from blue to yellow.

In bacteria (primarily the marine *Vibrio* species) and certain insects (the firefly, *Photinus pyralis*, and the click beetle, *Pyrophorus plagiophthalamus*), the bioluminescence phenomenon has been dissected to the point that the biochemistry and genetics of the light emission systems are known and have been exploited using genetic engineering techniques.

The bacterial *lux* gene system has been used extensively as a marker or reporter gene to track the movement of bacterial species, and to "report" the presence of chemicals as biosensors. In the latter case, the promoters controlling the synthesis of the light emitting complex and supporting enzymes must be removed and replaced by promoter elements sensitive to the chemical of interest. Whole cell biosensors have been developed that are sensitive to organic compounds such as napthalene and to metals including mercury. In the case of napthalene detection, such biosensors have been demonstrated to respond to as little as 1.5 ppm in 23 seconds under laboratory conditions.

Green Fluorescent Protein—Green fluorescent protein is a component of the light production system in the marine jellyfish, Aequorea victoria. Energy is transferred from the photoprotein aequorin to GFP, generating light. GFP fluoresces bright green upon excitation with light in the blue and UV wavelengths (360 – 400 nm excitation maxima). The gene for GFP has been cloned and extensive recombinant DNA modifications have been performed by a variety of researchers to produce variants that are excited at different wavelengths (including red light) and emit in the blue, red, and yellow wavelengths. A potential advantage of using this particular reporter system is that additional genes are not required (the bacterial lux system requires a suite of genes and utilizes host-supplied energy to generate light) for response. However, the protein (or cells expressing the protein) must be excited by light in the correct spectrum for fluorescence to occur, which predicates a detector system with a monochromatic light source and PMT, photodiode, or CCD camera to detect the emitted fluorescent light. We are not aware of GFP-based biosensors that have been developed for environmental contaminants to date.

Construction of Lux and GFP-Responsive Biosensors—A key component of a specific bioluminescent or fluorescent sensor is the sensing component. For this class of sensor, genetic elements called promoters, which normally switch on cellular responses to environmental stimuli (chemical contaminants, for instance), are fused to the "reporter" gene system. In the arsenic-responsive sensor we are developing, components of the bacterial arsenic resistance operon (ars) are fused to the lux and GFP reporters. Bacterial resistance to arsenic occurs through the recognition and active pumping of arsenite anion out of the bacterial cell. Resistance is inducible (meaning that gene expression of the resistance system is turned on) by arsenite anion, through binding of arsenite to the arsR-coded repressor protein. This in turn causes the repressor to fall off the promoter sequence, leading to gene expression. The organization of arsenic resistance genes from the resistance plasmid R46 (sequenced by our laboratory several years ago) is depicted schematically in Figure 2.

To construct the two reporter systems we propose, the R46 promoter and arsR gene have been excised from a clone created at the INEEL, pIRC 120, using the restriction endonuclease SphI. The fragment was further processed with PstI, and blunt ended with DNA polymerase Klenow fragment. This

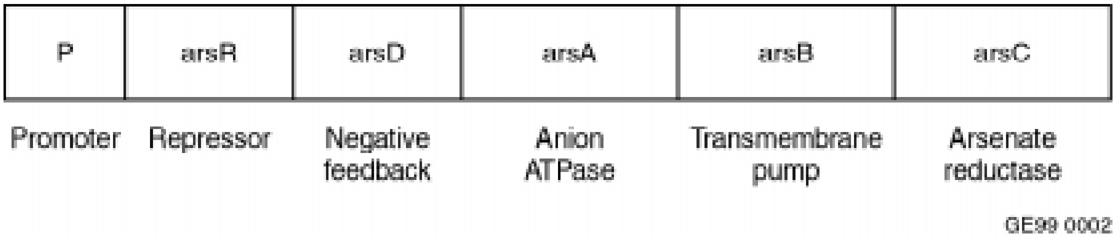


Figure 2. Organization of the promoter and structural genes for arsenic resistance in R46. Functions of the various structural genes are indicated.

response element has been fused with the lux gene cassette that is present on the plasmid pUCD615 (obtained from C. Kado, University of California, Davis). The GFP-responsive clone is being produced in a similar manner by fusion to the GFP reporter gene found in pGFPuv (Clontech, Inc.). A diagram of the constructs is presented in Figure 3.

Immobilization of Whole Cell Biosensors and Antibodies—Finally, immobilization of the biosensors to a glass microscope slide will be accomplished by conventional biochemical means. Glass surfaces can be activated using dichloromethylsilane, yielding reactive groups above the glass surface to which proteins can be crosslinked. Alternatively, glutaraldehyde has been used successfully to attach whole cells and proteins to glass and plastic surfaces. A conceptual view of the finished array and integration of detection hardware follows in a later section.

Inkjet technology—Another novel method under consideration is the use of inexpensive inkjet printer technology to lay down chemical compounds in patterns required for multivariate chemical microsensors. These devices are capable of placing very small quantities (~$3x10^{-6}$ mm^3) of any of several fluids at precise locations. The Epson Stylus Photo EX is an excellent example, boasting 1,440 x 720 dpi resolution and carrying six independent ink reservoirs. An additional advantage of the Epson printer for our application compared to the Bubble Jet type (Cannon, Hewlett-Packard), is that the ink ejector mechanism uses piezoelectric micro-pumps rather than thermally vaporized ink to eject the ink drop. We believe that the types of organic compounds we envision using will, in general, be adversely affected by the heat generated by the Bubble Jet method.

Epson provides guides for developing custom drivers for the print mechanism so that one could, for instance, lay down multiple drops at one location, and later lay down more after a suitable drying time to build up thicker layers. These custom drivers provide substantial control over the patterning process, and the simultaneous presence of six potentially unique compounds in the cartridges is also attractive.

One attractive possibility for building prototype micromachines and microsensors would be to use the Epson printer to lay down patterns of materials that could then be converted to durable structures. These materials might include metals (from soluble salts), sol gels, etc. A typical silicon sol gel might be laid down in complex patterns to build up walls, cavities, channels, etc., which would then be thermally converted to silica. One could use the metal compounds to apply conductive electrodes, electrical contacts, etc. so as to rapidly prototype even complex microsensors. Another intended use will be to use the printer to create patterns of sensor compounds on selected substrates. This will simplify the manufacture of prototype microsensors and ensure rapid turnaround times for new designs.

Self Assembly for Manufacture of Complex 3D Microstructures—Although not a major portion of this project, self assembly techniques may have considerable impact on the complexity of micro machines and sensors that can realistically be produced. One approach to this problem involves the assembly of simple building blocks into more complex structures using any of several biologically derived adhesive systems, including antibody/antigen pairs, DNA/RNA pairs or Biotin/Actin pairs.

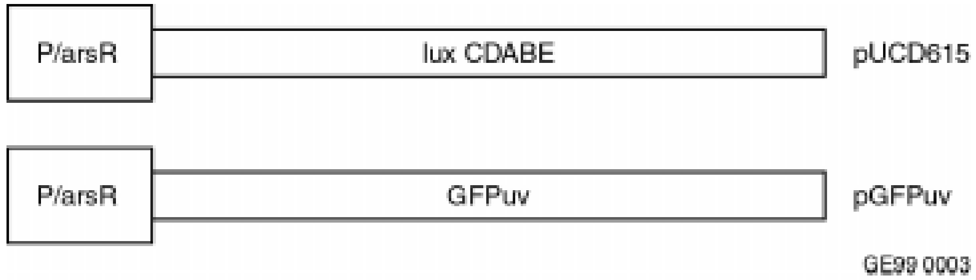


Figure 3. The lux construct.

Conceptually, one would apply one of an active pair to the surface on one component, and the other member of the pair to the surface of a second component. One would then rely on the natural tendency of these molecules to lock together to cause mating surfaces of the two components to become attached. It is assumed that only a statistical portion of the assemblies would be correct and that some post assembly inspection step would be necessary to choose those that have assembled correctly and reject or reprocess those that have not.

Instrumental Enhancement of Ion Mobility Spectrometry. IMS is a highly sensitive trace analysis technique for organic analytes. It is a gas phase atmospheric pressure ionization technique in which analyte ions are separated based on their shape and charge in an electric field region that is swept by a bath gas. Although (IMS) is becoming commonly utilized for a number of applications, such as the detection of explosives, drugs, and chemical warfare agents, specific limitations in the technique have suppressed widespread acceptance of IMS as a viable field analytical tool. The instrument has advantages in its high sensitivity to a number of chemical functionalities and the ability to be produced at a reasonable cost in a fairly small and rugged package.

The major limitation of the technique is the low inherent instrumental resolution, which affects the ability of the instrument to discriminate between analyte peaks and other compounds present. This is perhaps the most compelling reason that the technique has not received more widespread use in field analytical applications. An increase in system resolution would have a significant impact on the utilization of the technique. Applications would benefit from the increase in resolution by a decrease in misidentified analytes. IMS usage on environmental monitoring problems in many cases is limited to low complexity samples, due to the inability of the instrument to resolve peaks from analytes of interest from those arising from the background of a complex matrix. To enhance the viability of IMS in environmental monitoring and other application areas, a focus of this work was to identify mechanisms for enhancement of the resolution of IMS instrumentation.

Although IMS is very sensitive to a wide variety of chemical functionalities (with picogram detection limits), many utilization scenarios dictate the need for even more sensitivity. When an instrument is being used for critical applications, such as the detection of chemical warfare agents or explosives, the sensitivity level could mean the difference between life and death. The ability of a technique to measure the smallest mass of analyte possible in a very large sample is paramount to a number of other applications also, including environmental monitoring scenarios where the regulatory limits are very low. Therefore, a second major focus is the enhancement of the sensitivity of the instrument.

The necessity of this work can easily be illustrated by the fact that nearly all of the commercially available IMS instruments on the market are nearly identical in design to those outlined in the original IMS patents. Although IMS has progressed in the maturity of the electronic components and computers for data acquisition and control, the geometry and physical implementation of the drift tube has remained relatively unchanged. Research in IMS in the recent past has focused on applications and increasing the performance of the instrument through design changes. A few exceptions to this are the Fourier transform IMS from Washington State University and the ion trap IMS from Ion Track Instruments

Microinstrumentation. The microinstrumentation task had several objectives: analyzing the ability of the INEEL to contribute to the field, determining opportunities within the EM program for applying microinstrumentation, and using the results of those two analyses to build a program in microinstrumentation. No current capability exists at the INEEL to carry out the design steps nor the fabrication steps to build microinstruments. Part of the analysis was to understand where the INEEL could best use its current capabilities, without investing millions in microfabrication infrastructure.

FY 1998 Accomplishments

Introduction

The following section describes the work and achievements of the various program subelements for the first six months of this effort.

Membrane Characterization by Mass Spectrometry. This is a new instrumental analysis capability for the INEEL. A Varian Saturn Gas Chromatograph (GC)/Mass Spectrometer (MS) was modified for this work (Figure 4). The GC was removed from the system and replaced by a special valve, port, and probe assembly. This was a commercial unit that has an integrated pump and heater system specifically designed for the MIMS type of activity. The unit was mounted and tested, and then work was begun. In all of the testing reported below, aqueous solutions were used. 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 aliquot of the solution containing the desired analyte dissolved in water is inserted into the feed system via the injection port. The aliquot of material passes across the membrane and then exits to a collection unit.

Polydimethylsiloxane (PDMS) rubber is the material most highly studied in MIMS applications. Because there is much published data, this material was selected for use as a baseline system check. Many runs were made using toluene (T), ethanol (ETOH), 1,1,1-trichloroethylene (TCE), isopropanol (IPA), methylethylketone (MEK), and in some cases tetrahydrofuran (THF) as the target analytes. Temperature, concentration, feed flow rates, polymer thickness were among the parameters varied during

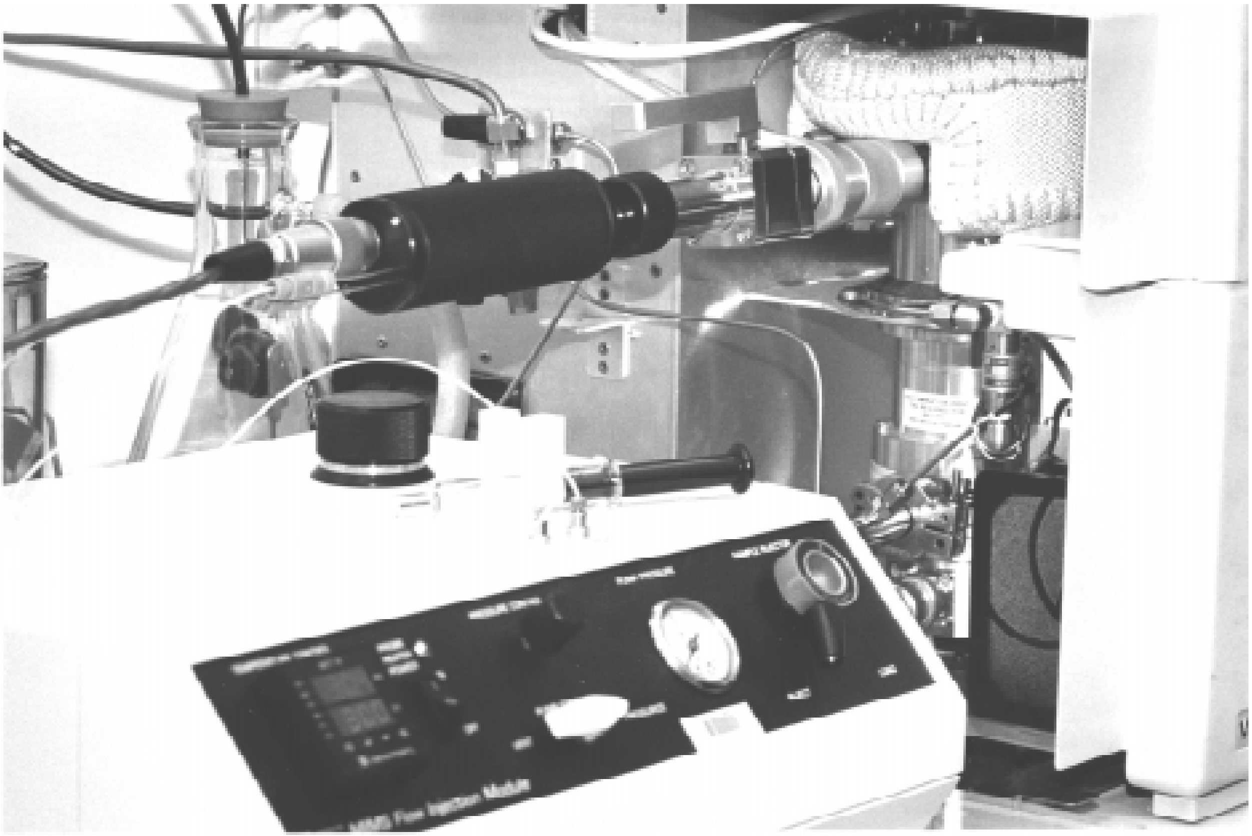


Figure 4. MIMS instrumentation.

the runs. More than 100 runs were made with toluene on PDMS. The detection limit measured for toluene was 20 ppb, for TCE 10 ppb, for IPA 2 ppm, and for MEK 2 ppm. The reported values were measured on different types of spectrometers and are well within an order of magnitude of literature-reported values.

Once the baselining activities were completed, the testing of phosphazene polymers was begun. One of the first membranes was a partially fluorinated phosphazene (TE-1-75). This polymer made a nice film and was tested against THF, MEK, TCE, IPA, and T. All of these substances were easily detected. This polymer showed a lower limit for toluene and a higher limit for TCE than did the PDMS. This good result indicates that polymers other than PDMS may be very useful as sensor/concentrators for analytical techniques.

The two figures at the end of this section (Figures 5 and 6) show the large concentration ranges that are easily detectable with the MIMS setup—over five orders of magnitude. The figures indicate that the phosphazene materials have close to the same sensitivity as does the silicone rubber for toluene. The figures give the typical response curves to a one ml injected sample.

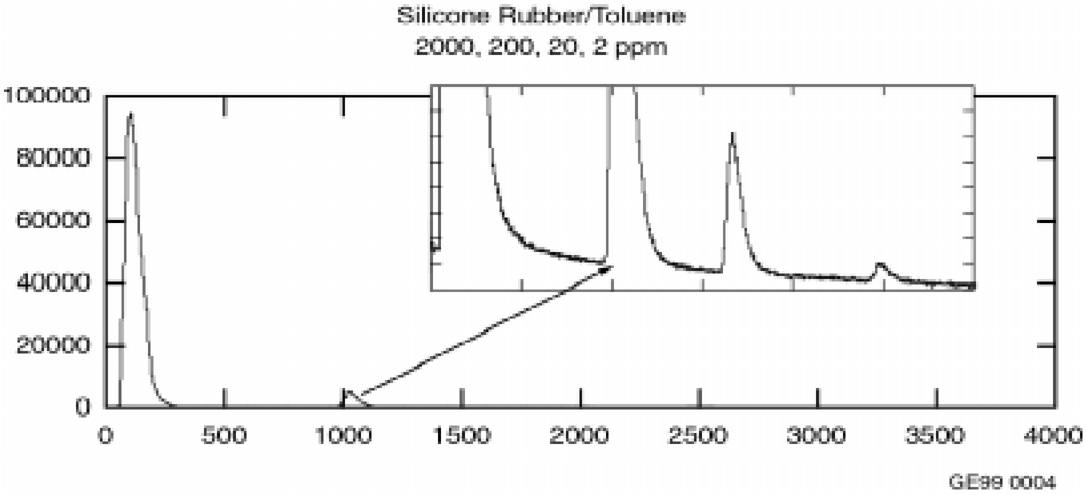


Figure 5. Response for toluene using a silicone rubber membrane.

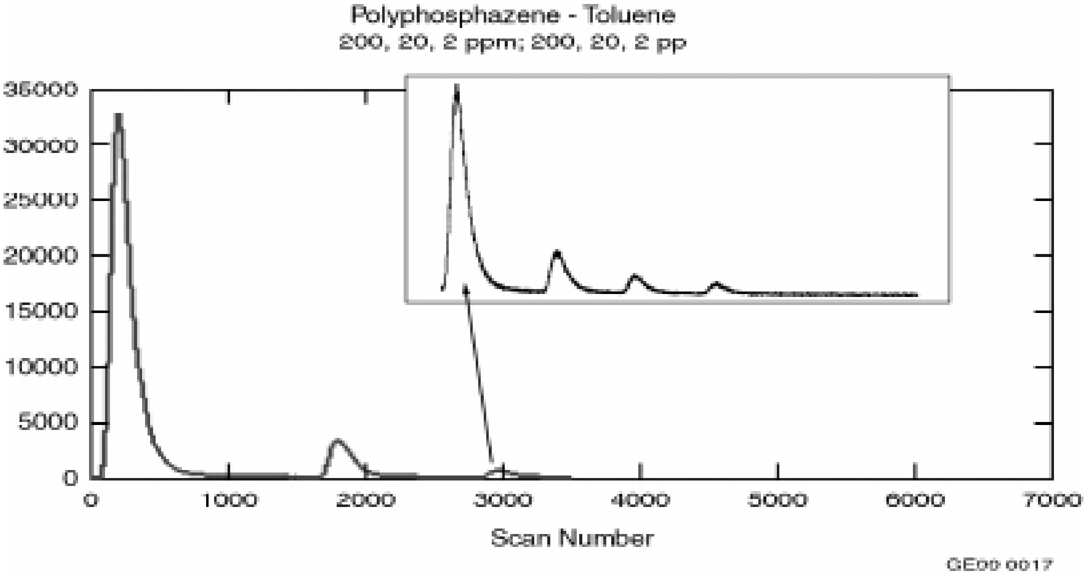


Figure 6. Response for toluene using a polyphosphpazene membrane showing ppb sensitivity.

Two polymers having the same chemical formula but with different molecular weights were tested. The higher molecular weight material did not pass anything. The lower molecular weight showed a high flux with most of the analytes tested. This was an important result, because it gives another parameter (molecular weight) that might be varied in order to fine tune a polymer's performance as a membrane for sensor applications. The detection limits were higher than those of the PDMS. Other polymer testing is ongoing.

Microlasers.

Development of Inhibitors—An attempt was made to develop a battery of chemical inhibitors that would effectively differentiate representative bacteria that collectively express all five of the known toluene-degradative pathways. This has been accomplished with three inhibitors: 1-pentyne, phenylacetylene, and 5-bromo-2-furoate.

It has previously been shown that phenylacetylene is a flourogenic substrate for strain F1 that can be used to fluorescently label individual cells expressing active toluene-degrading enzymes. Therefore, phenylacetylene is a fluorogenic substrate for strain F1, a colorigenic substrate useful for colonies of strains F1 and G4, and a selective inhibitor for strain KR1.

The inhibition of growth of KR1 by phenylacetylene was further studied by examining the effects of structurally related compounds. Equal amounts of the following compounds were added to vials inoculated with KR1 to study the effects on growth: toluene, styrene, 1-phenyl-1-propyne, 3-phenyl-1-propyne, and 4-ethynyltoluene. From these data it was seen that the triple bond was required for activity, which was greatest when the triple bond was in a terminal position. Phenylacetylene exhibited the greatest inhibition of growth of KR1.

Inhibition by phenylacetylene is likely to result from monooxygenase-catalyzed epoxidation of the triple bond, yielding a highly reactive oxirene/carbene intermediate. The various toluene monooxygenases hydroxylate toluene in different positions due to specific binding orientations of toluene at the active sites of the enzymes. Therefore, we expected that nonaromatic substrates might exhibit different selectivities relative to phenylacetylene. 1-Pentyne was chosen because it is the smallest alkyne that is in the liquid state at room temperature and hence is easily handled. We showed that a 1-pentyne/toluene mixture (5% v/v pentyne) provided a selective growth condition different from phenylacetylene/toluene mixtures. With 1-pentyne, strain KR1 was unaffected, whereas growth of strains G4 and PKO1 was completely inhibited. Strains F1 and mt-2 were unaffected by pentyne. Note that with the monooxygenase-containing strains G4, PKO1, and KR1, phenylacetylene and 1-pentyne have opposite effects on growth.

During FY-98, the previously mentioned experiments have been refined and repeated to obtain data of publishable quality. A few experiments remain to be completed and will be completed by the end of September.

During FY-98, we obtained a mutant derived from mt-2 that had apparently lost the plasmid encoding the TOL pathway. Strain mt-2 also contains a chromosomally encoded pathway that allows growth on benzoate, but not on toluene or *m*-toluic acid. The mutant was able to grow only on benzoate. We have also obtained from a colleague an *E. coli* host that has been transformed with DNA encoding a part of the TOL pathway; the encoded enzymes are actively expressed. The mutant and *E. coli* transformant will be instrumental in tests designed to further characterize the inhibition.

Procurement, Integration and Testing of a Nanosecond Resolution Time-Resolved Fluorimetry System—A fluorescence lifetime spectroscopy system was designed, integrated and tested in the laboratory. The system uses an IBH Model 5000 Coaxial Flashlamp as the excitation source. The flashlamp unit contains an evacuable discharge chamber with the discharge controlled via a thyratron tube. The unit is designed to operate with different gases and gas mixtures producing high stability nanosecond pulses in the 180 to 780 nanometer spectral ranges at repetition rates up to 100 kHz.

Detection of the fluorescence lifetimes is performed by time-correlated single photon counting. In this scheme, shown schematically in Figure 7, a small fraction of the light is directed to a fast photomultiplier, where a sync pulse starts a time-to-amplitude converter (TAC). When an emission photon is recorded by the photomultplier, the TAC is stopped. This signal is proportional to the time from the excitation event to the first photon recorded. The signal from the TAC is then digitized and sent to an appropriate channel of a multi-channel analyzer. The process is repeated until the analyzer represents the number of photon events as a function of time. An example of data collected with the system is shown in Figure 8.

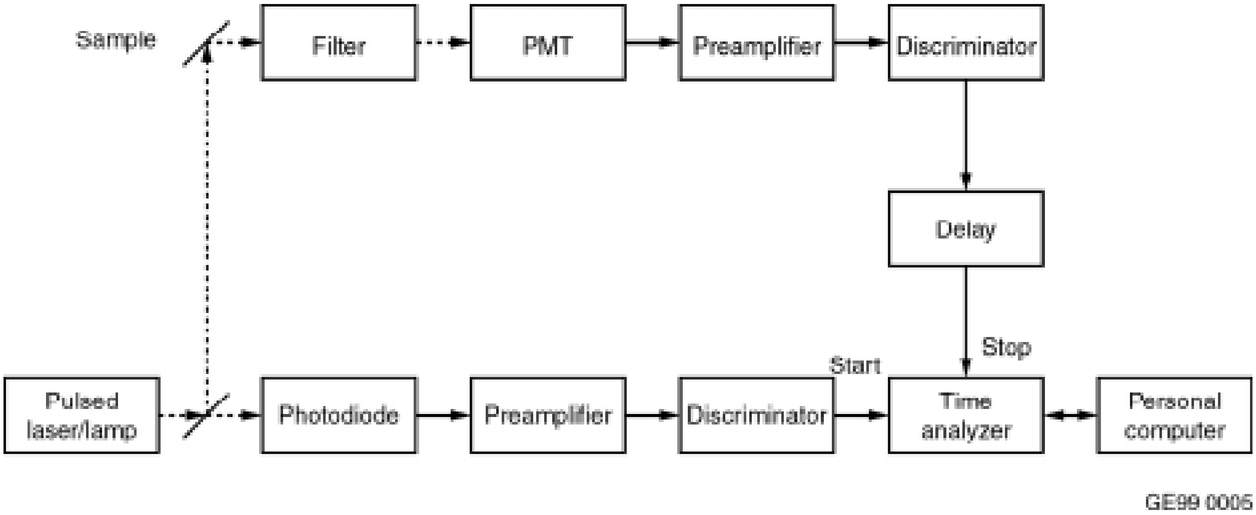


Figure 7. Fluorescence lifetime measurement equipment configuration.

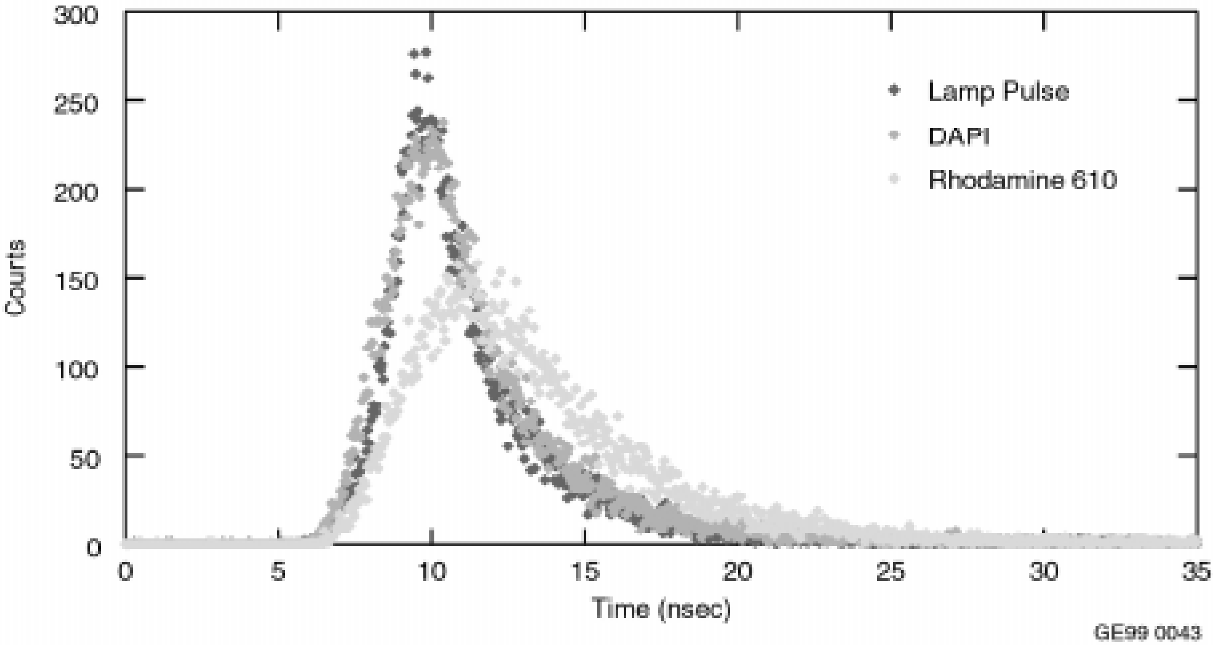


Figure 8. Fluorescence lifetime plots.

Biosensors.

Bioluminescent Sensor Concepts—Arsenic-responsive genetic elements have been fused to the bacterial luminescence gene system and the resulting construct is undergoing testing for response (light emission) to arsenic. A parallel GFP construct is nearing completion and will also be tested for fluorescence emission in the presence of arsenic. Antibodies directed against toluene have been obtained and are being immobilized in a planar array with the arsenic biosensors. Commercially available arsenic-responsive genetic elements have been fused to the bacterial luminescence gene system and the resulting construct is undergoing testing for response (light emission) to arsenic.

Optomechanical hardware to detect light and fluorescence emission from the planar array have been designed based on commercially available components, and assembly awaits receipt of the components from the various vendors.

Inkjet Technology—We have acquired the Epson Photo EX printer and are currently studying the driver software and how one might use the existing mechanism to lay down desired chemical or mechanical patterns. It may prove that modifications will have to be made to solve such problems as replacing the somewhat curved paper path with a straight through path that will accommodate thicker substrates. Issues concerning chemical compatibility with the print head are also of interest.

Self Assembly for Manufacture of Complex 3D Microstructures—Design of a simple silicon microstructure (box) has been finalized and fabrication by a commercial silicon fabrication lab will be performed in collaboration with Washington State University, as funding and availability allows.

Instrumental Enhancement of Ion Mobility Spectrometry. A large volume ion mobility spectrometer originally designed for ion-molecule reaction studies was configured as a testbed instrument (See Figure 9) for this project. This instrument was ideal for the experiments, as all aspects of the instrument were easily accessible for reconfiguration. Parameters that could be easily changed included: ionization source type and geometry, collector type and geometry, drift voltage spacial arrangement, drift length, carrier gas type and flow, drift gas type and flow, Tyndall gate implementation, and drift cell pressure. Seven high voltage power supplies, three waveform generators, and two high speed high voltage pulse generators were used to vary the implementation and timing of the gate pulses, collector grid potentials, source pulses, and the drift field. Control and timing of these fields were used to develop the resolution enhancements.

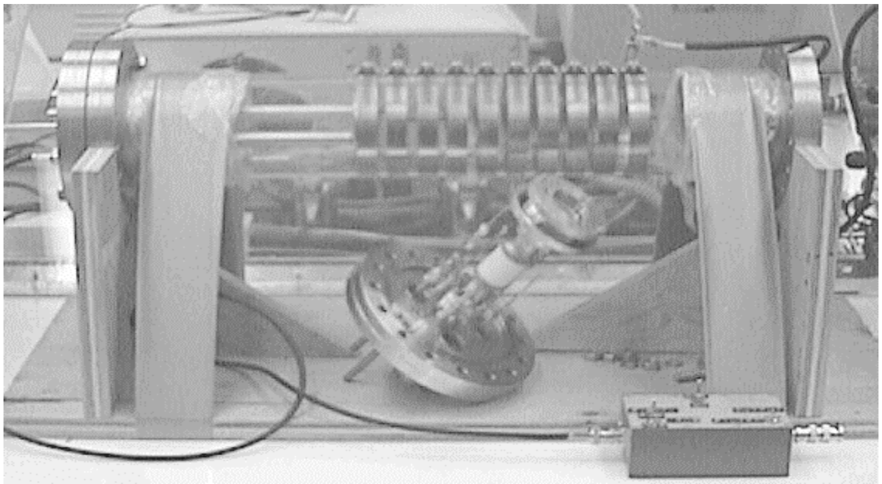


Figure 9. Testbed Ion Mobility Spectrometer.

The optimal resolution is defined initially by the gate or source pulse width introduced into the drift region. Resolution is degraded from optimal values by a number of physical mechanisms: diffusion, drift voltage inhomogeneities, space charge effects and gate depletion effects. Resolution increases can therefore be induced by the reduction of these pulse broadening mechanisms.

Resolution losses due to diffusion cannot be implicitly controlled. The use of higher drift voltages lead to a decrease in the effects of diffusion, since the ions travel the fixed drift length faster and thus are under the influence of diffusion effects for a shorter period of time. This phenomenon is stated in Fick's law, where the diffusive mass transfer is demonstrated as being a function of time. The remaining mechanisms of band broadening aside from diffusion and space charge effects have a dependence on the electric field implementations in the instrument, and thus should be susceptible to manipulation.

The largest contribution to bandwidth originates with the gate pulse. In most cases, field inhomogeneity and gate depletion effects on band width are very minor compared to the size of the gate pulse. Typical IMS systems utilized drift lengths of 5 to 15 cm and electric fields around 200 V/cm. This results in typical analyte drift times in the 10 to 15 millisecond range. Gate pulse widths are typically 200 to 500 microseconds. This results in ion utilizations of 1% to 5%. Gate pulse widths can be reduced to enhance resolution, however, this results in even lower ion utilization efficiencies and therefore lower sensitivity. In many analytical applications, the losses in sensitivity eventually become unacceptable. Also, gate depletion effects limit the sensitivity and resolution at very narrow gate pulses. Resolution enhancements studied in this work used modifications of the electric fields in the instrument connected with both the drift field and the gate trigger pulse to reduce the bandwidths.

Figure 10 illustrates an example of the resolution gains that can be made by manipulation of the electric fields involved with the gate pulse. Timing of electric field manipulations is critical to maintaining not only resolution, but sensitivity. However, by using the main gate trigger pulse to synchronize the timing, very few timing problems occurred. By changing the placement and the timing of the additional electric field pulses to the system, resolution enhancements of up to 10% can be realized. Initial optimization experiments have shown a mobility dependence upon the resolution increase, meaning that much higher resolution gains may be possible when optimization of the applied field for a specific mobility range is done.

Aside from modifications of the gated ion packet as described above, elimination of the ion gate altogether would serve to reduce the band width effects brought about by this function. These experiments centered on the use of a potential well to provide the ion pulse. A potential well can be

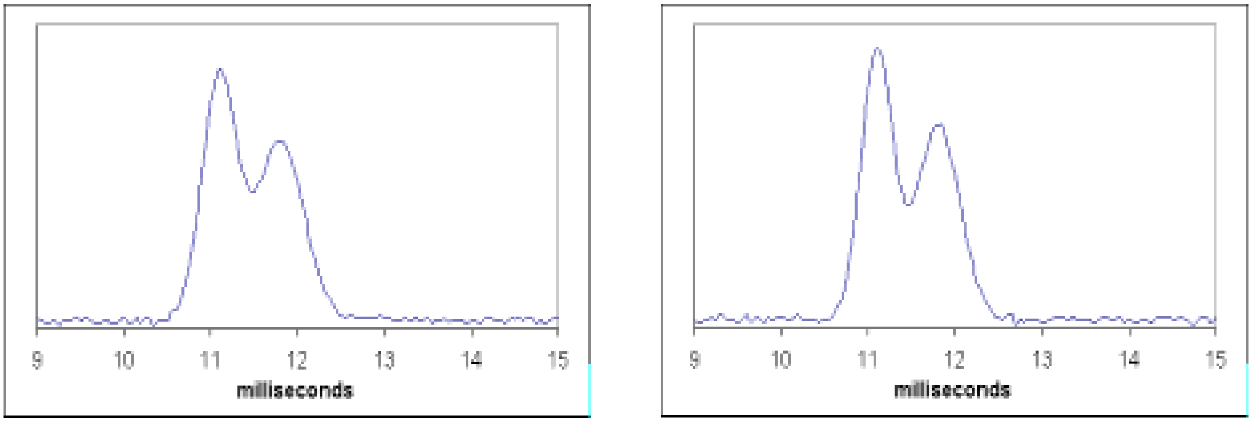


Figure 10. Resolution enhancement by additional triggered electric field, before addition (left) and after (right).

added in place of the gate near the source region; this well can be toggled to provide an ion collection and pulse generation mechanism. Figure 11 illustrates the potential well implementation in comparison to the electric field profile. The potential well voltages used were 100 to 500 volts below the value used in the linear field IMS arrangement (1,800 volts at the implementation point). The performance of this setup was disappointing from a resolution and noise standpoint, although the ion gate could be effectively eliminated. The broad peaks resulting from this arrangement were contributed to space charge repulsion effects brought about by high ion densities in the potential well. This problem was diminished greatly by the addition of another electric field to counteract the space charge repulsion effects.

Peak shapes, and thus resolution, can be enhanced by varying the timing and amplitude of the additional electric fields. This is most likely due to the reduction in space charge repulsion effects in the potential well. Figure 12 illustrates the peak shapes resulting from both the potential well only setup and modified potential well arrangement. The top curve is the ethylamine analyte peak using only the potential well setup. The bottom curve is the analyte peak using the modified potential well arrangement containing the additional electric field. The latter setup allows for peak widths approaching those of gated IMS systems. The top curve illustrates the effects of space charge repulsion on peak shape. Also of note is the rising baseline on either side of the peak. Charge repulsion effects also lead to a bleed of ion current from the potential well. This effect increases with time as more ions are collected and thus result in a rising baseline. Further optimizations of the voltages would most likely result in even narrower band widths than illustrated in the bottom curve.

A novel corona discharge based ionization source developed by the laboratory was configured into the testbed instrument. The goal of using this source was to enhance resolution by creating and injecting a very narrow pulse of ions into the drift region. It is envisioned that this type of ionization source may be able to replace the typical radioactive source for creating ions and also displace the ion gate for providing a narrow ion band to the drift region via pulsed mode of operation. Figure 13 shows the initial prototype discharge ionization source. The initial experiments appeared successful, with a very narrow pulse from the collector being observed on an oscilloscope. Discharge was triggered with 10 microsecond, high voltage pulses to the source and was clearly observable by the naked eye inside the testbed instrument. Aside from the potential resolution gains, it is envisioned that the pulsed discharge source may provide sensitivity gains, as the ion currents from discharge processes are much greater than

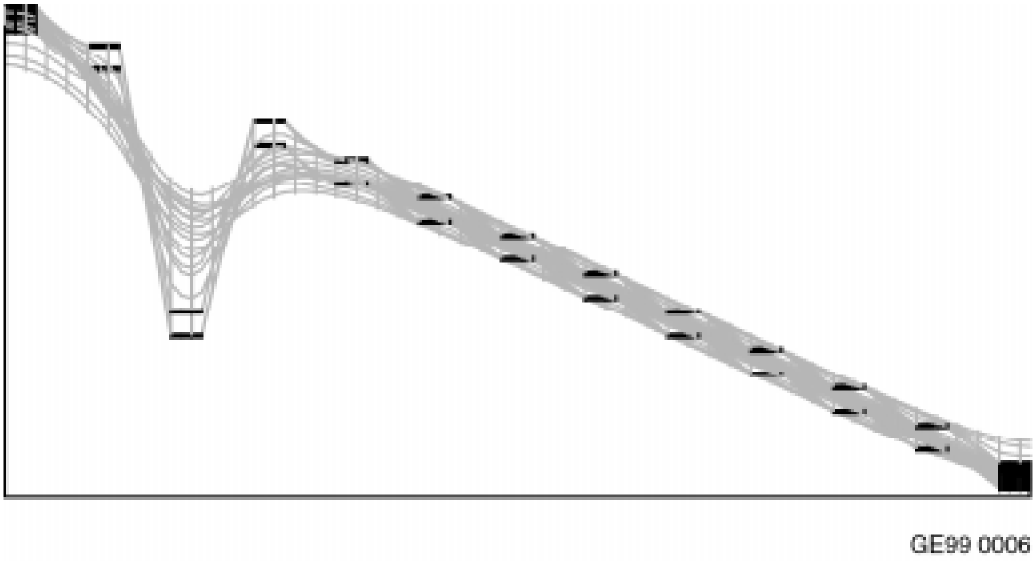


Figure 11. Potential well implementation into IMS drift field.

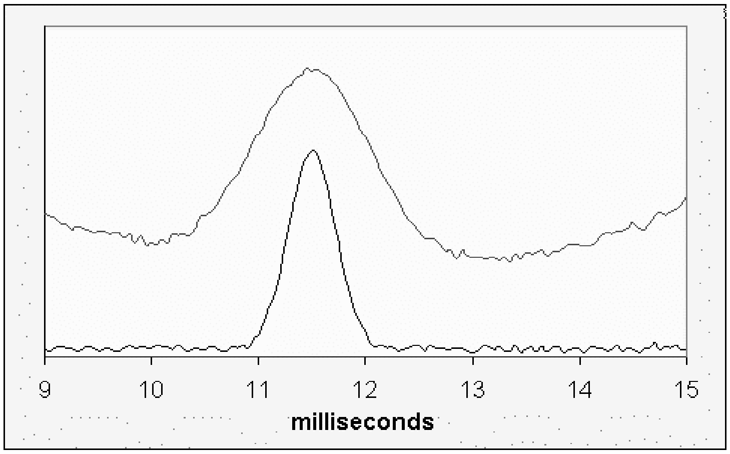


Figure 12. Effects of potential well and the modified potential well on analyte peak shape.

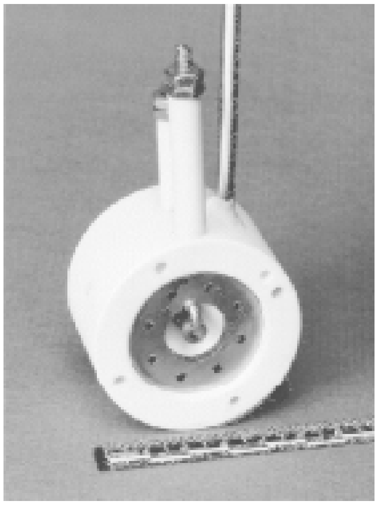


Figure 13. INEEL prototype corona discharge source.

low energy beta particle ionization as is typical in IMS. The experiments revealed very narrow bandwidths from the pulsed mode of operation. Sensitivity was not as high as expected, but this could be from an unoptimized extraction of ions away from the source and into the ion drift region. Theoretically, the discharge source should provide a much higher ion density than the ^{63}Ni source typical to IMS.

Much of the sensitivity in IMS with ^{63}Ni ionization comes from the efficient ionization processes, and the limits on sensitivity are often based upon instrumental design parameters. The 1% to 5% ion utilization is a major source of signal loss, and thus the replacement of the ion gate with a pulsed source such as the discharge source mentioned above should help that factor significantly. Ion-ion recombination also reduces the available analyte ion pool before detection. Diffusion and space charge repulsion of ions to the drift tube walls also accounts for significant signal loss. Finally, at the ion detection end, the faraday plate is a century old and very noisy method of ion collection. A reduction in the effects of any of these detriments would allow for enhancements in sensitivity.

Electric fields were implemented to attempt to utilize a higher percentage of the ions. A number of simple experiments were done to determine the effects of focusing the ion pulse at various times and locations in the drift tube. Although sensitivity could be greatly enhanced fairly easily, these enhancements nearly always came at a steep cost in resolution. The major reason for this stems from the fact that ions do not macroscopically accelerate under the influence of an electric field at atmospheric pressure. Therefore, ions that undergo a large amount of focusing cover a longer path than less focused ions, at nearly identical velocities. This results in broadening of the ion pulse. This phenomenon is very much unlike mass spectrometry, where the highly focused ions in a vacuum accelerate such that they cover the additional path length in about the same time frame as less focused ions, thus allowing for spatial focusing without substantial band broadening.

The ion mobility experiment is often a trade-off between resolution and sensitivity, this is also true with the attempted enhancements. It is envisioned, however, that sensitivity and resolution can be optimized for each analyte individually when necessary via the additional electric fields. Also, the performance of two experiments back to back on a specific sample, one with enhanced resolution and one with enhanced sensitivity, provides a large amount of useful analytical information. It is envisioned that some of these enhancements will find their way into commercial instrumentation as the mechanisms are further studied and the patent applications are filed.

Microinstrumentation. Many research groups are engaged in developing a wide variety of microinstruments. A survey of a cross section of ongoing activities was performed. A report was prepared that summarizes many activities in the field of microinstrument development.

A wide variety of detection schemes are being explored. However, even with the variety of detection schemes that are being researched, integration at the micro level is one of the biggest issues that needs to be overcome. The current operational microchip systems are not integrated systems at the micro scale. Cohe, Nikiforov, and Parce (Caliper Technologies Corp.) have reported a microchip system for kinetic enzymatic analyses. While all of the necessary chemistry is performed on the microchip, the detection scheme involves fluorescence microscopy. In a similar vein Walker, Morris, Johnson, and Burns (University of Michigan) have described a microchip system on which ions are separated by isotachophoresis and the separated species detected by Raman spectroscopy. In this case the detector was a Raman microscope capable of sampling nanoliter volumes.

Currently, it appears that microchip analyzers require most of their system support from macroscopic entities such as the controlling computer, spectrometers, and other types of signal conditioners. For the most part the microchips are serving as small chemical reactors or separators with signal detection and processing occurring off-chip. The same can be said for the microelectrochemical arrays. The driving electronics for the stripping voltametry or amperometry as well as the measuring circuits appear to be standard macroinstrumentation.

A host of issues are associated with trying to create integrated packages in which all of the necessary functions occur on-board at the chip level. It is not too hard to use micromanipulators to place system elements in an operational configuration for a demonstration. It is quite another thing to consider this practice as a means of producing thousands of low cost microanalytical instruments. In the sample management area, as mentioned above, mechanical means of moving samples through the system as opposed to using electrophoresis or electroosmosis will mature at a later date. The use of shape memory alloy drivers or piezo electric drivers necessary for sample movement will require developing strategies for creating the structures on the same substrate as the sensors via lithographic or LIGA techniques. It is not yet demonstrated that the materials that need to be employed for these diverse functions are mutually compatible in lithographic or LIGA processing techniques. In addition there can be substrate-structure compatibility problems.

A particularly serious issue that needs to be addressed for EM applications is that of calibration. The concept of autonomous microinstruments sitting out in the field or positioned down a sampling well, transmitting information concerning the chemistry of their surroundings, is one that is easy to imagine.

However, in the world of environmental measurements, there are rigorous prescribed methodologies for sample analysis with stringent QA requirements. In order for any substitute method to be acceptable it will have to demonstrate equivalent performance to the prescribed standard. Some means of self-calibration will have to be devised for any autonomous microinstrument in order for it to demonstrate equivalent performance.

The fact that chip level devices are being used for various types of assays, as reported above, lends credence to the possibility of fully integrated devices at the chip level. A great deal of work remains to understand the types of elements that can be integrated, to understand and resolve the materials issues, and to understand the design and processing strategies.

There are a number of areas in which the I^3SCM Program can participate effectively in the development of new sensor technology. The majority of current efforts appear to be focused on biological and biomedical applications. There is not a lot of emphasis on developing sensors that target environmental contaminants. Pursuing the development of microinstrumentation to support EM’s needs does not look like it will be a redundant effort.

One area in which there does not appear to be much activity is in the area of microsampling. As a result of the data gathering, collation, and analysis that has occurred, it appears that it will be fruitful to capitalize on our experience in membrane separations and membrane characterization to do research in the area of microseparations. The initial forays into this area have led to an agreement with Sandia National Laboratory to exchange information on permeable membrane sampling (INEEL) and surface acoustic wave (SAW) devices (SNL).

A report describing the potential opportunities for the deployment of microsensors within EM operations was prepared. The data for the report was drawn from several sources, i.e., Characterization, Sensors, and Monitoring Technologies Cross-cutting Program (CMSTCP) staff, STCG needs documentation, and the Subsurface Containment Focus Area’s Decision Analysis for Remediation Technologies (DART) database and analysis tool.

The DART tool was developed for the SubCon Focus Area by the INEEL. It contains data concerning the principal contaminants and contaminated soil volumes for most of the operational units (OUs) and waste area groups (WAGs) within the Complex. Using this tool, the top 25 contaminants (both radioactive and RCRA) were identified in terms of the largest volume of contaminated soil. In excess of 10^8 m^3 of contaminated soil have been identified, in addition to which there are areas for which the characterization is incomplete or not started.

The STCG Needs data, while not specifically calling for the development of microinstrumentation, implied a need for such devices. There will be a need over a broad range of remediation operations for instrumentation to monitor the progress of the cleanup activities.

An analysis of the data from these two studies indicated that there were opportunities for the development of microsensors for the detection of RCRA metal contaminants such as mercury, chromium, arsenic, and others. The organic contaminants of greatest concern include tetrachloroethylene, chloroform, toluene and a number of others. This was the information that led to the direction for the biosensor work described above.

Summary

Given the fact that the program has only been active since mid-February, a great deal of progress has been made, and its momentum will carry the program smoothly into its 1999 activities. The overarching theme of the I^3SCM program is to carry out research that will lead to less expensive chemical analysis instrumentation that is more readily usable in field applications. The program elements that have been described above may not appear to be integrated at this point when looking at the details of the work thus far. However, as the work progresses, results from each of the tasks will be examined for integration into the other activities. In an iterative restructuring process, the program will take on an integrated appearance as input from the results of each task have influences on the other tasks. For example there are plans to examine the use of the membranes that have been characterized as sampling interfaces for the IMS. The microlaser will be investigated as a narrow pulse photoexcitation source for the IMS to provide enhanced molecular resolution that may provide an opportunity to produce a smaller portable instrument. The microlaser has the possibility of being an efficient excitation source for the microarray biosensors. The program will evolve in this manner over the next several years.

Membrane Characterization by Mass Spectrometry

There are two aspects to this program. One is establishing a new capability at this laboratory and the other is the developing new materials that have unique characteristics that make them useful for sensing/analysis. Both aspects are going well. A capability for performing membrane introduction mass spectrometry has been established. The baseline studies show that the technique is performing up to expectations. The development of new and useful membranes for a variety of applications is being facilitated by use of the MIMS capability. Existing materials are being investigated so that a performance/structure relationship can be developed and from that new formulations can be designed, manufactured, and tested. Already differences have been observed for INEEL materials that indicate they may be better than existing materials for selected sensing/concentrating applications

Microlasers

This project has provided new chemical tools for the detection and differentiation of aerobic toluene-degrading bacteria, many of which also degrade trichloroethylene. The tools include selective inhibitors of bacteria using specific toluene-degrading pathways and fluorogenic substrates for biodegradative oxygenase enzymes. Data needed to validate these tools are nearly complete for two inhibitors, but will require further funding for the remaining inhibitor and probes. A nanosecond resolution time-resolved fluorescence system has also been integrated in the laboratory for testing. These probes and inhibitors will be useful in laboratory tests and *in situ* measurements of microbial biodegradative activities using nutrient-diffusing devices coupled to microfluorimeters. Additional studies are needed to demonstrate the utility of the probes and inhibitors with nutrient-diffusing devices. Also, further studies are required to refine this technology and render it widely applicable for environmental monitoring.

The technology will provide monitoring capabilities that are not possible by other means and are invaluable for monitoring biodegradative activities at contaminated sites. The technology can be used to detect bacteria, to determine which nutrient amendments to groundwater will stimulate desired bacterial growth, and to determine if inducible/ repressible biodegradative enzymes are expressed under natural conditions. Also, the devices could be used as biosensors to detect chemicals in the groundwater provided that bacteria added to the device (artificially) respond to the chemical by synthesizing enzymes that catalyze a probe transformation (wild-type bacterium including environmental isolates) or bioluminescence (genetically engineered bacterium).

Biosensors

The following list summarizes progress to date:

- Arsenic-responsive genetic elements have been fused to the bacterial luminescence gene system and the resulting construct is undergoing testing for response (light emission) to arsenic

- A parallel GFP construct is nearing completion and will also be tested for fluorescence emission in the presence of arsenic

- Antibodies directed against toluene have been obtained and are being immobilized in a planar array with the arsenic biosensors

- Optomechanical hardware to detect light and fluorescence emission from the planar array have been designed based on commercially available components, and assembly awaits receipt of the components from the various vendors

- Design of a simple silicon microstructure (box) has been finalized and fabrication by a commercial silicon fabrication lab will be performed in collaboration with Washington State University, as funding and availability allow

- A piezoelectric-based inkjet printer has been obtained for evaluation as a method for depositing the biological and mechanical materials in the demonstration array and sensor housings

Instrumental Enhancement of Ion Mobility Spectrometry

Ion mobility spectrometry is a highly promising technique for organic trace analysis in the field. Limitations in resolution is the major barrier to widespread application for environmental monitoring. Incremental enhancements of the instrumental resolution via minor design changes have been demonstrated here as feasible. Numerous opportunities for patent disclosures have been identified from this work where performance increases were demonstrated. It is envisioned that similar design changes will occur in the future, making the IMS technology more mature, and more applicable to the myriad of environmental applications awaiting the arrival of a portable high performance trace organic analysis system.

Microinstrumentation

The microinstrumentation activities are primarily focused on the opportunities in the area of microsampling as well as coordinating with the activities in the biosensor research. A probable need for the development of a variety of sensors that will have application in remediation activities has been shown. A synergistic relationship with SNL has been developed that will be beneficial to both programs. The INEEL will benefit from SNL’s years of experience in SAW detector technology. SNL will benefit from INEEL’s experience in membrane separations. In addition the INEEL in its position as the EM Laboratory will be able to provide a demonstration platform for the SNL Microchem Lab when it is ready for demonstration in an EM environment.

INTELLIGENT NONINTRUSIVE METHODS FOR CHARACTERIZATION

T. J. Roney, D. C. Kunerth, J. C. Determan, G. K. Becker, and T. A. White

Scope and Objectives

This project is addressing several basic physics and data processing issues in characterization of spent nuclear fuel (SNF) and other nuclear waste and industrial inspection problems. Successful nonintrusive inspection often involves making a series of independent measurements and applying prior knowledge, intelligent processing of information, and automated decision-making. This project is studying two independent nonintrusive technologies, eddy current and x-ray imaging, and several approaches to data interpretation with the overall objective of advancing the state of the art in nonintrusive sensing and intelligent data processing while enabling specific improvements to spent nuclear fuel inspection, transuranic (TRU) waste characterization, and industrial inspection. Specific objectives include developing a greater understanding of potential spent fuel inspection/characterization problems and making advances in intelligent processing of waste characterization data. The studies in this project will resolve characterization issues, select specific characterization problems to approach, investigate the unique physical phenomena affecting the measurements, develop selected sensors, and develop interpretation and processing algorithms. There are four specific tasks: Spent Nuclear Fuel Characterization Issues, Intelligent Interpretation of Waste Characterization Data, Electromagnetic Material Characterization, and Imaging in Constrained Environments.

Technical Accomplishments

Background and Motivation

INEEL plays a leading role in processing and storage of spent nuclear fuel and nuclear legacy wastes for the DOE complex. Characterizing the contents of nuclear material containers, and characterizing container integrity, are critical for retrieval, processing, transporting, interim storage, and ultimate disposal of nuclear material. Characterization of waste drums containing transuranics has been an active area of research for 15 to 20 years and substantial advances have been made; characterization of SNF containers is relatively new. While there is important common ground between characterizing nuclear waste containers and characterizing spent fuel (e.g., container sizes and shapes; physics of inspection; and extensive, exacting regulatory control), there are also major differences (e.g., source term; criticality concerns; internal/external configurations; effects of moderators, poisons, and corrosion; and longer term controls on storage and disposal). Characterization methods for SNF containers cannot be fully developed until regulations governing waste acceptance criteria are completed. Our work is driven by the need to characterize SNF containers, but it will also be useful in characterization of nuclear waste containers and industrial applications requiring multimodality nonintrusive inspection.

Characterizing SNF containers includes verifying the presence of fissile material; quantifying the fissile material and radionuclides; identifying moderators and poisons; establishing the configuration of fissile material, neutron moderators, and neutron poisons; verifying the integrity of barriers (cladding and container); determining internal and external environmental conditions (pressure, moisture, corrosion); and identifying void spaces and the presence of organic materials. The ability to make measurements is severely impacted by physical limitations (e.g., configuration of material and storage environments), high radiation backgrounds, material properties, and complex signals. It is desirable to develop measurement instruments and data interpretation and decision-making tools that will be useful for characterization during retrieval and processing as well as during long-term interim storage and disposal.

FY-98 Technical Accomplishments

This project has four tasks: Spent Nuclear Fuel Characterization Issues, Intelligent Interpretation of Waste Characterization Data, Electromagnetic Material Characterization, and Imaging in Constrained Environments. The first task, Spent Nuclear Fuel Characterization Issues, will identify the problems to be addressed by the other three. Through literature reviews, discussions with personnel in the National Spent Fuel Program and the INEEL Spent Fuel Program, and interactions with INEEL personnel, we are developing a list of the SNF characterization problems that are expected. The second task, Intelligent Interpretation of Waste Characterization Data, is developing methods to automatically process and interpret characterization data to improve efficiency and reliability in the waste characterization process. The current emphasis is on expert systems to process neutron assay data. The remaining two tasks will improve individual measurements. The Electromagnetic Material Characterization task is using intelligent processing techniques to improve the interpretation of broadband eddy current data. The Imaging in Constrained Environments task will develop imaging algorithms for situations with limited access or high radiation backgrounds.

Spent Nuclear Fuel Characterization Issues

This task is identifying the characterization requirements that will govern processing, transporting, and disposing of SNF so that we can identify the advances in nonintrusive sensing that will be needed to meet those requirements. While the types of characterization needed are fairly well known (e.g., assays of radioactive material and evaluation of the structural integrity of SNF and its containers), the levels of accuracy and precision, details to be reported, and criteria for decision making are not known because the waste acceptance criteria have not been established. This report summarizes the relevant information learned to date.

Roughly 70,000 metric tons of SNF are destined for a repository. The majority of SNF consists of fuel assemblies from commercial reactors and DOE fuel from defense production reactors, naval propulsion reactors, domestic and foreign research reactors, and commercial reactors. Only about 10% of the total is DOE waste, and roughly half of that is in a glass waste form. Thus only 5% of the repository will be filled with DOE SNF. However, DOE SNF is sufficiently different, in terms of configuration and enrichment, from commercial SNF to generate strong interest and oversight. Also, because the Nuclear Regulatory Commission (NRC) is not familiar with DOE fuels, it is expected to be very conservative when generating requirements for licensing for transportation and for long-term storage. (Transportation requirements are expected to be the most stringent ones facing SNF.)

Two major concerns of the NRC will be criticality and release of radioactive substances. Some questions to be answered are:

Is the fuel damaged and deteriorating?

Are the fission products dispersible?

Are there fission gases between the fuel and cladding?

Are there corrosion products?

Many SNF assemblies are currently stored underwater, but within 5 years the majority of SNF will be in dry storage containers. Ideally, containment vessels are designed to last a long time; however, experience has shown that fuel may decompose or crumble within a container and containers may also degrade. For dry storage casks, proof will be required that a 40 to 60 year lifetime is viable, i.e., chemical and physical stability is assured. Proof that casks will not degrade due to cladding deterioration (attack from the inside out), halide stress corrosion, or pressurization may be secured by either developing long-term monitoring devices or by experimentation. It may also be necessary to prove that there are no changes in an older container (i.e., lifetime extension of older casks). Interim storage licensing presents issues as well; for example, a site must show that it can monitor fuel or that monitoring is not required.

The INEEL also has several projects that may require new characterization technologies. For example, all fuel currently in wet storage must be moved to dry storage by 2003. This raises concerns regarding the condition of material to be retrieved, its physical and chemical stability during processing, and its condition at the beginning of dry storage. Processing Three-Mile-Island, Advanced Test Reactor (ATR), and Fermi reactor fuels presents unique problems. For example, the aluminum fuel plates from ATR have 50 to 70 mil cooling channels that may be filled with sludge. The Fermi fuel is doubly canned aluminum that may have suffered microbially-induced corrosion on the inner wall of the outer shell, allowing water to penetrate the can.

There are both opportunities and challenges for inspection systems. The size, shape, material properties (e.g., high-density shielding), and content of SNF canisters and casks pose challenging problems to conventional nondestructive inspection systems. Storing multiple SNF assemblies in one container complicates the deployment of inspection systems. High radiation backgrounds may interfere with measurements and corrupt measurement hardware. Due to the variety of assemblies, storage containers, and configurations, much of the inspection hardware will likely be tailored to specific storage situations.

Possibilities for intelligent processing also exist. Because a high level of quality assurance is required, and most processes go through extensive review, it will be important to reduce the number of decision points and for systems to make decisions on their own. For example, spent fuel drying stations are currently manually operated. It may be beneficial to automate the drying stations to control the drying parameters.

Intelligent Interpretation of Waste Characterization Data

This task is concerned with intelligent processing methods for automated interpretation and validation of waste characterization data. Technical review of waste characterization data, though warranted because of present day waste assay system capabilities, is labor intensive. Hence, it is desirable to have an automated system perform this review. An automated system for technical review of waste characterization data must be capable of providing a comprehensive waste assay data assessment, and must be reproducible, auditable, and compatible with the overall throughput requirements of the waste characterization process. Efforts in FY-98 sought to test expert systems as viable methods for technical review and decision making in transuranic waste characterization. A prototype has been developed and two presentations at national meetings resulted from this work.[1,2] The evaluation of expert system technology for this application began by developing a system capable of automatically generating fuzzy rule sets from data. Its performance compares favorably with similar rules developed manually.[3]

The overriding goal of this work is to investigate and apply expert system technology to waste characterization data. In particular, this year we are interested in nondestructive assay (NDA) data from transuranic waste drums. One aspect of this work is finding methods to facilitate knowledge acquisition, as this is the primary bottleneck in expert system development. Broadly, this work falls into the category of machine learning, which is the study of methods by which knowledge can be acquired by a machine, either automatically or with minimal human supervision. The latter branch of machine learning, supervised learning, may be further divided into statistical/inductive techniques and example-based techniques. Both of these methods are being explored. Statistical/inductive techniques locate patterns in training data and abstract these patterns into general rules. Example-based techniques extract useful features from specific examples and either generalize the example solution into a rule for broader application or remember the example in sufficient detail to be useful solving future problems. In particular, case-based reasoning (CBR) for learning NDA data by example is being explored. Statistical/inductive techniques are frequently used within CBR systems for learning indexing schemes for efficient case storage and retrieval, thus such systems may used on their own to generate classification rules, or within the context of other systems.

A system for generating fuzzy rules for classification problems from training data has been developed. The method employs a fuzzy clustering algorithm to develop fuzzy rules relating the inputs and outputs in the training data. A key parameter of this algorithm is the number of clusters. At one extreme, every training point becomes a cluster, the training data is learned perfectly, but no generalization to other data is possible. The other extreme, a single cluster, is of little use in learning to distinguish among the examples. Cluster validity indices are used to quantify the compactness and separation of data clusters, and to identify when the appropriate number of clusters has been chosen. A genetic algorithm employing the Xie-Beni fuzzy clustering validity index has been used to locate a set of good parameters for the fuzzy clustering procedure. Each data cluster serves as a rule prototype; back-propagation is then used to find the optimal shape of these clusters with respect to the training data. Parameters that describe the shape and position of these clusters in the input data space are then used to form fuzzy membership functions describing the degree of inclusion of each data point in each cluster. Each optimized data cluster is thus transformed into a fuzzy rule composed of a fuzzy membership function for each input dimension. The set of fuzzy rules act together to produce a classification of the input data. Thus, patterns present in training data are abstracted into a set of rules for classification. The Xie-Beni index,[4] S_{XB}, has been proposed for evaluating the validity of fuzzy clusters. This index is the ratio of the compactness of the clusters (a measure of the variance of the data points from the centers of the data clusters) to the square of the minimum distance between the cluster centers. In general, small values of S_{XB} indicate well-formed data clusters, provided the number of clusters does not approach the number of data points in the training data. Therefore, S_{XB} may be used as a component of the objective function.

An objective function employing the information embodied in S_{XB} was sought. Initial tests were performed on an objective function consisting of the reciprocal of S_{XB}, such that maximizing the objective function resulted in a small value of S_{XB}. While some good solutions (high-performance, minimal rule sets) were produced, the system did not converge to these solutions, but instead degraded to lower performance solutions before converging. Figure 1 illustrates why this occurred, and suggests a solution. The coordinate axes in the figure are related to the components of S_{XB}: the minimum inter-cluster distance squared, vs. the reciprocal of the compactness. The reciprocal of compactness was chosen so that the maximization of the quantities on both axes resulted in a small value of S_{XB}. Using only the reciprocal of the Xie-Beni ratio to control the genetic algorithm selects solutions purely on the basis of possessing a small ratio. The Xie-Beni ratio is at a minimum in the central corridor of the plot in Figure 1, so solutions from this region of the plane will be favored. Good solutions, however, must possess both good inter-cluster separation and a small measure of compactness, not just a small ratio of these values. The only solutions in the favored corridor that meet these criteria are those most distant from the origin. Hence an objective function based only on the Xie-Beni index favors a few good solutions, and many mediocre ones.

Figure 1 also suggests a better form for the objective function. The arch of solutions maximally distant from the origin contains the solutions that have either maximal separation, maximal compactness, or a reasonable combination of both. From a genetic standpoint, this arch represents an ideal gene pool. The solutions in the arch possess desirable components of the final solution, and “breeding” these solutions should result in continual improvement in the population. This arch represents the solutions

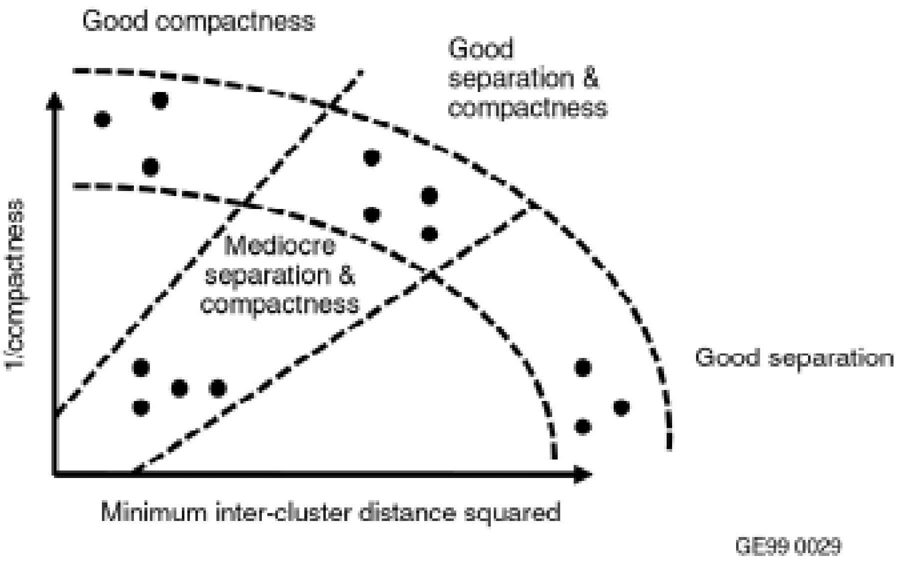


Figure 1. Analysis of genetic algorithm objective function behavior.

favored by a multi-objective optimization method known as Pareto optimization.[5] Pareto optimization ranks data into subsets of approximately equal worth with respect to multiple criteria. The criteria used were the reciprocal of compactness and the minimum inter-cluster distance squared. Maximizing these quantities tends to reduce S_{XB}.

The rule generation system was trained and tested against a set of assays classified by a panel of NDA experts. The confidence in the assay results for each of three modes of operation (Passive System, Passive Shielded, Active) was rated on a scale from zero to ten, where zero represented no confidence and ten represented high confidence in the measurement.

Expert system performance for each NDA measurement mode indicates the level of agreement between the manually classified test set and the classifications produced by the expert system. A simple function was used to roll system performance into a single number:

Performance = $\sum 4a + 2b + c$

where

a = number of data points in test set agreeing within 10%

b = number of remaining data points agreeing within 25%

c = number of remaining data points.

Table 1 lists the "selected," maximum, and average solution performance at convergence for each of three measurement modes for assay of waste drums. The "selected" solution was the "best" solution according to the Xie-Beni index criteria. The selected solution had maximum performance in two out of three cases, and was a high performer in the remaining case. The expert system resulting from rules formed from this clustering procedure can achieve a high, if not optimal, level of performance.

Table 1. Values of Xie-Beni index and performance at convergence.

	Selected	Maximum	Average
Passive System			
Performance	194	194	193.6
Xie-Beni	0.095	0.095	0.101
% Correct	90	90	—
Passive Shielded			
Performance	184	186	184.0
Xie-Beni	0.101	0.108	0.116
% Correct	80	82	—
Active			
Performance.	178	178	177.6
Xie-Beni	0.046	0.046	0.047
% Correct	78	78	—

Work with expert nondestructive assay personnel at INEEL to develop the manual set of rules resulted in a good understanding of the current data review process and established a positive relationship with the potential end users of this technology. Future work will address the acquisition of knowledge from isolated examples, where statistical/inductive techniques employing training data would be impractical. A hybrid system combining case-based reasoning and expert systems will be applied to quality assurance of waste drum NDA measurements. The expert system component is used to flag drums with significant anomalies in the data, a CBR component will be used to remember significant data review cases and use these to reason about solutions to new situations encountered during data review.

Electromagnetic Material Characterization

The objective of this task is to develop real-time, multifrequency eddy current data inversion techniques for automated material characterization and nondestructive evaluation. Automated and real-time material characterization applications range from spent fuel and radioactive waste storage containers to protective metal coatings and composite or graded metal structures. Data processing tools are essential for automating pulsed/multifrequency eddy current technologies and for obtaining real-time characterization. Two approaches can be used for data inversion, model based and neural networks. Model-based approaches are relatively complicated, making implementation difficult and often slow, but they have the potential to address complex material conditions. Neural networks are simple and fast, but limited by the training methodology and scope. The nature of the application will determine which inversion approach is best. Thus, basic knowledge of both methods is desired.

Evaluation of neural networks as a means to invert/extract data began in FY 1998. The measurement of waste storage drum wall thickness was selected as the application to be tested. Prior work had shown the potential of the pulsed eddy current technique for measuring the wall thickness of carbon steel storage drums, and thereby determining drum integrity, but improved data processing technologies are needed to fully exploit the information obtained from this multifrequency technique. Various test parameters need to be addressed, including wall thickness, probe wobble, magnetic permeability/electrical conductivity variations, and probe lift-off due to labels, surface corrosion, or dents. The contributions from all of these parameters are integrated into the eddy current response and need to be separated to adequately extract the desired information, i.e., wall thickness. This problem is illustrated in Figure 2, which shows the similarity of the eddy current responses to different wall thicknesses and to a small amount of probe lift-off. Lift-off significantly impacts the ability to make a reliable thickness measurements.

The evaluation of the ability of neural networks to accept and process data obtained from the pulsed eddy current drum integrity measurements began by acquiring neural network development packages and developing neural networks based on pulsed eddy current data sets. Typical results of the initial training of a neural network to predict the thickness of a waste storage drum are shown in Figure 3. This was a feed-forward, two-layer network with 100 sigmoidal neurons in the input layer and a linear neuron in the output layer. The predicative capability of the neural network degrades, as would be expected, for increasing lift-off. This is the result of reduced electromagnetic coupling and sample penetration. The difficulty in correct prediction for the full data set shown in Figure 3 is primarily due to a time shift of the basic signal response for a given thickness as shown in Figure 4.

Within this initial study, the neural network was primarily used as a pattern recognition system. This network was not designed to exploit the physical (physics) properties of the signal that lead to an accurate prediction of the drum's thickness. Figure 4 implies that instead of training a neural network to use the normalized raw data signal, a preprocessing technique that attempts to predict the signal's overall shape might be used. Such a method might try to fit the original data signal with a high order linear/nonlinear function whose coefficients can be better used to train the neural network to predict thickness. By preprocessing the signal into a basic shape, the temporal signal effects shown in Figure 4 can be better overcome. Furthermore, reducing the neural network's inputs allows it to be configured and trained more quickly and robustly. Although additional work is required, the basic results indicate that neural networks have the potential to address the multiple test parameters.

In FY 1999, work on neural networks will continue with efforts to further refine the algorithms being evaluated and to demonstrate a system that can acquire and process pulsed eddy current signals in real time via neural networks. The approach will be to use a PC-based digital signal processing (DSP) board capable of implementing various neural network algorithms. The DSP board will be integrated with data acquisition boards to construct a computer-based data acquisition system for testing and demonstration and for a development platform for automated inspection systems.

The model-based inversion effort will begin by developing an electromagnetic inversion model that can be used to obtain conductivity profiles, i.e., $\sigma(x)$. With the exception of the work performed by Siegfried et al,[6] eddy current data inversion research has been directed towards the reconstruction of isolated defects and not electrical conductivity profiles. The proposed work limits the inversion problem to conductivity in an effort to address bulk material characterization problems such as general erosion/corrosion, microstructure (e.g., case hardening/work hardening and thermal damage), structure (e.g., thickness of coating or laminations), and process parameters (e.g., temperature gradient profiles). The intent is to develop a real-time/near-real-time inversion algorithm. Inversion efforts outside the INEEL will be investigated and collaborations initiated to permit INEEL model development and testing.

Imaging in Constrained Environments

The main thrust of this task is to develop the capability to acquire, process, and reconstruct three-dimensional image data in situations that are presently intractable due to factors such as configuration limitations or high radiation backgrounds. It is likely that this type of imaging capability will be required

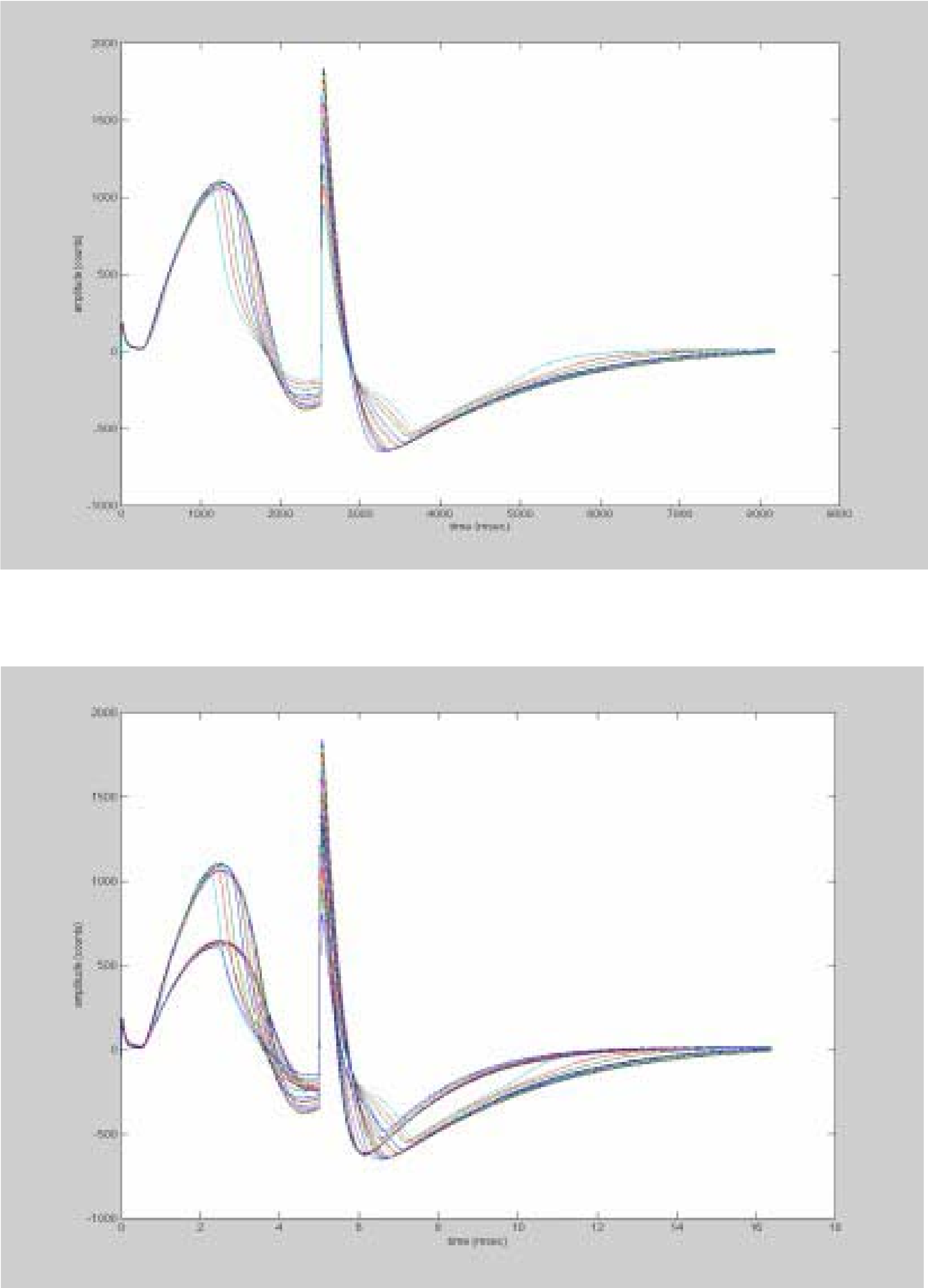


Figure 2. Pulsed eddy current response to variable sample thickness (top, transducer is on the sample surface) and to two different lift-off conditions (bottom).

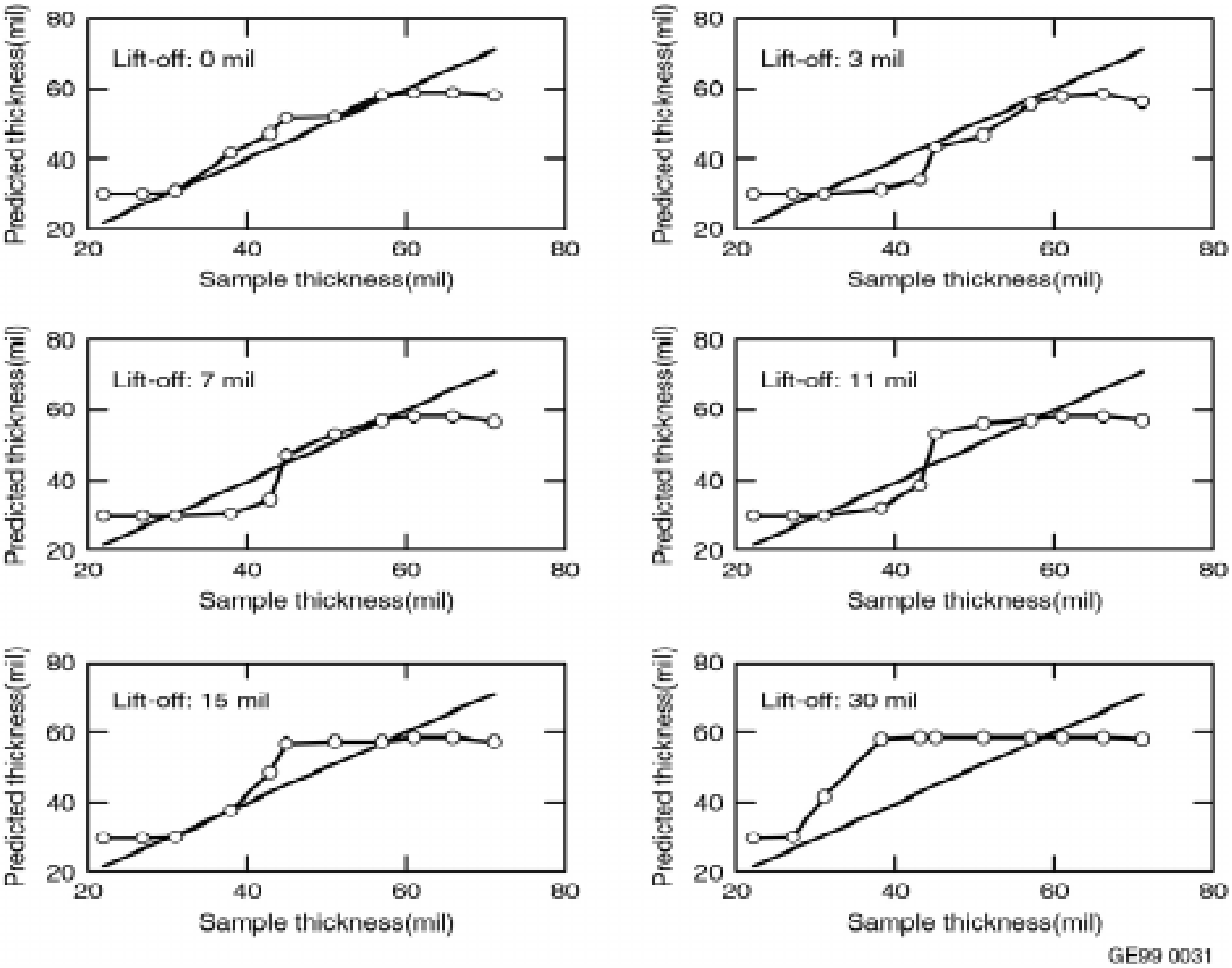


Figure 3. Initial neutral network results for predicted thickness with increasing lift-off (from 0 to 30 mil).

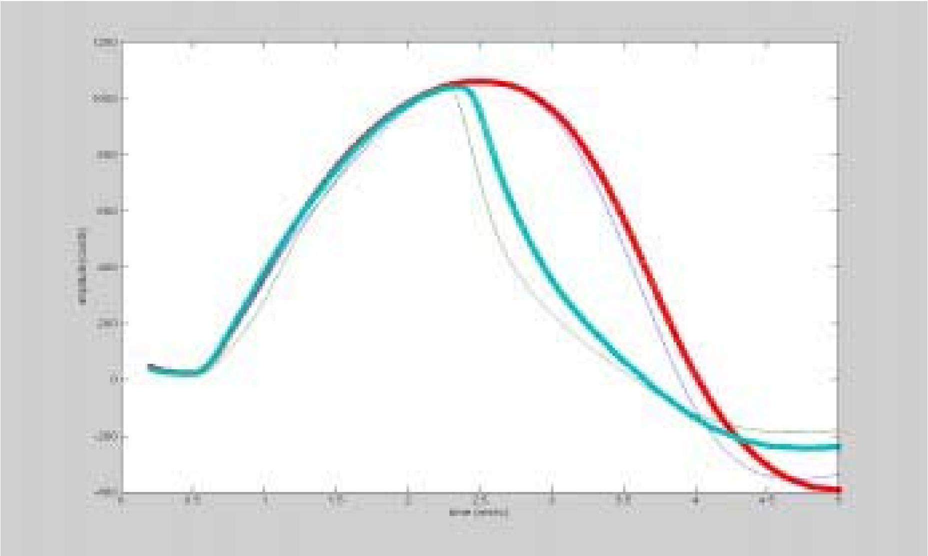


Figure 4. Comparison of normalized signals for maximum and minimum thickness for two different lift-off conditions.

for stored spent fuel, as well as being useful for industrial imaging configurations such as objects moving rapidly on a conveyor. In FY-98, several steps were achieved, including the acquisition and implementation of an amorphous-silicon area detector and initiation of a collaboration with the Medical Imaging Research Laboratory (MIRL) at the University of Utah for the development of reconstruction algorithms, imaging alignment parameters, and characterization of 3D imaging systems.

To test limited data imaging systems, an experimental conebeam computed tomography (CT) system was developed. The system consists largely of components available from other imaging systems in the INEEL Digital Radiography and Computed Tomography (DRCT) laboratory and an amorphous-silicon (A:Si) area detector acquired under this project. The A:Si detector, the most recent development in area detectors for x-ray imaging, consists of an x-ray scintillation screen directly coupled to a photodiode array built into the amorphous-silicon array. The array consists of 2,304 x 3,200 individual elements and produces an image with 12 bits of dynamic range (4000:1) for each of 7,372,800 pixels. The detector is driven by software that runs on Windows NT. For the experiments in FY-98, the detector was mounted on a field-portable instrument being developed in the DRCT laboratory to inspect 155-mm chemical weapons shells. The arrangement is shown in Figure 5.

To aid in determining the alignment parameters for a prototype conebeam CT imaging system, a phantom object was constructed. The object consists of six, 6-mm diameter steel ball bearings held in a thin polyethylene disk; a drawing of the object is shown in Figure 6. The locations of the balls are more or less random, but the position of each ball is known exactly. The phantom object was placed in the imaging system and radiographs were acquired as the object was rotated through 360 degrees. The relative positions of the balls in the radiographs was determined and used with the known position of the balls (from the drawing) to determine system alignment parameters.

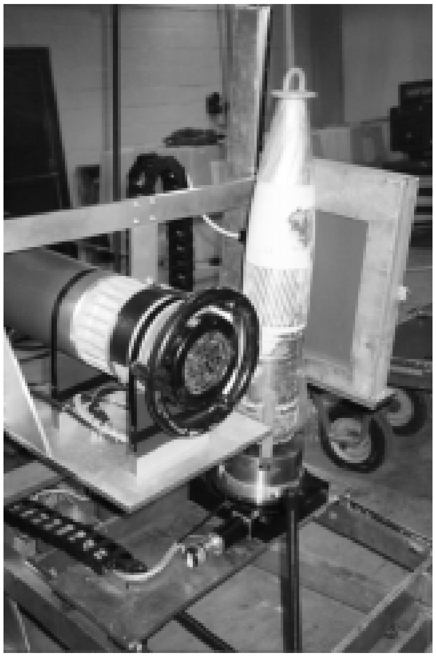


Figure 5. The amorphous-silicon x-ray detector mounted behind a 155-mm shell and a 300 kVp x-ray source. This system can manipulate source, object, and detector to acquire 3D data and was used to test the detector for 3D cone-beam-imaging applications.

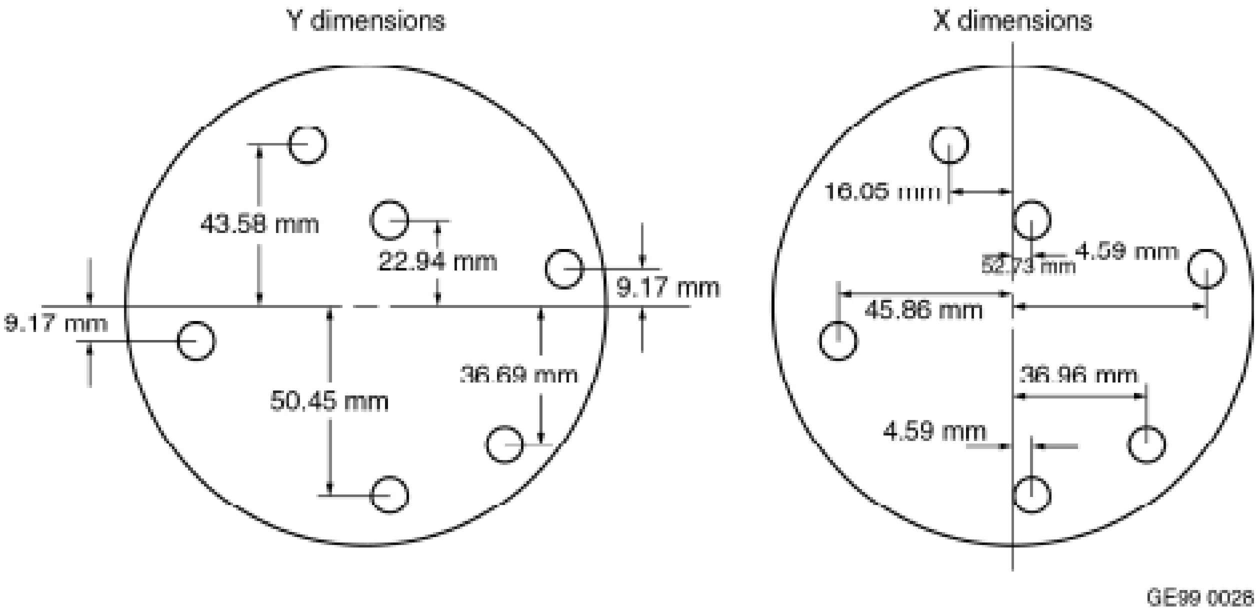


Figure 6. Drawing of the alignment phantom. The large circle is a polyethylene disk (~5-mm thick) that holds 6-mm steel ball bearings. The relative position of the balls is used in conjunction with a set of radiographs to determine system alignment parameters.

Using the parameters determined from the alignment procedure, the radiographs of the phantom were reconstructed into a 3D volume; a few slices from the reconstructed volume are shown in Figure 7. These reconstructed slices are perpendicular to a line running from the center of the x-ray source to the center of the detector. Since the plane containing the centers of the balls is skewed slightly with respect

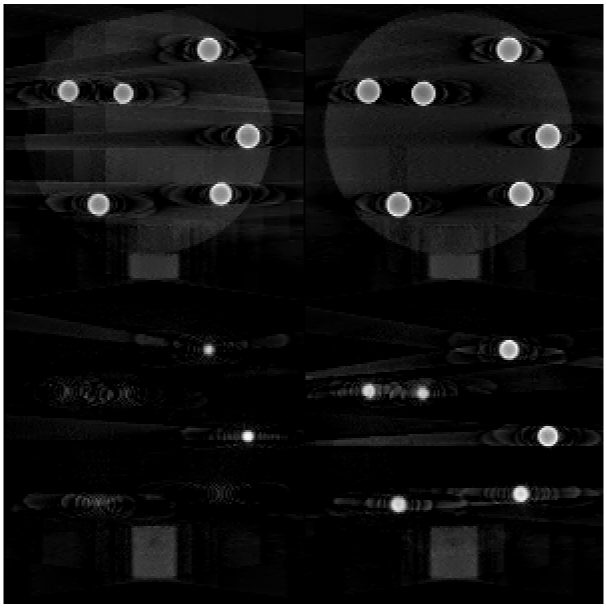


Figure 7. Four reconstructed slices of the alignment phantom. Slices are in planes parallel to the plane containing the center of each ball. Going counterclockwise from the lower left, the slice is in front of the balls, slightly touching the balls, in the plane containing the centers, and just slightly behind the plane containing the centers.

to the planes of the reconstruction volume (i.e., there is a slight misalignment of the object with respect to the imaging system), not all of the balls appear in each slice. Because of the limited number of angular samples (there were only 20 projections spaced over 360 degrees), there are some severe streaking artifacts in the reconstruction (which are more visible at different gray scales).

To further test the alignment of the imaging system, a set of radiographs of a darkroom clock were acquired. The data set has 200 views of the clock at 1.8-degree angular steps. The data were reconstructed into a 2563-voxel volume; the reconstruction took less than 30 min on a 200-MHz PentiumPro PC. In Figure 8 a radiograph of the clock is shown with four reconstructed slices. In the radiograph all of the internal components are superimposed and it is impossible to tell their relative front-to-back positions. The CT image makes their relative positions (a little) more clear.

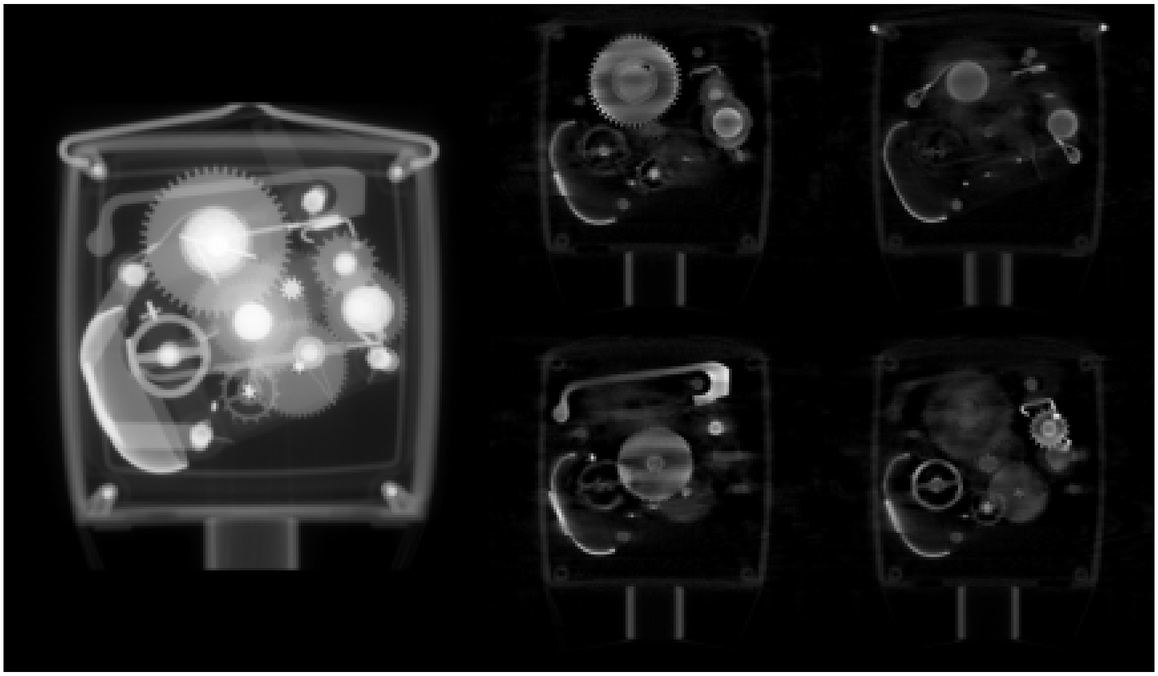


Figure 8. Radiograph (left) and four reconstructed slices (right) of a clock. The slices are parallel to the axis of rotation of the imaging system, and, moving from upper left to upper right, counterclockwise, are slices from the front to the back of the clock. Notice that in the radiograph all of the internal components are superimposed—it is impossible to tell the relative front-to-back position of the gears. The CT image makes the relative position (a little) more clear.

The collaboration with MIRL is proceeding along several lines, including development of a theory to estimate and correct for the geometric parameters in a 3D imaging system, limited data reconstruction algorithms, contour (or local) tomography, and imaging in a high radiation background. Their first report on geometric parameters will be provided in October 1998.

In FY-99, a laboratory system capable of emulating a variety of limited data configurations will be constructed and used to acquire data to test and develop limited data reconstruction algorithms.

Summary

This project consists of four major tasks that will contribute to solving the problem of characterizing SNF: understanding spent nuclear fuel characterization issues, intelligent interpretation of waste characterization data, electromagnetic material characterization, and imaging in constrained environments. Progress has varied within the individual tasks.

It is clear that the Nuclear Regulatory Commission will apply stringent standards that will greatly affect characterization requirements for SNF, but the waste acceptance criteria and related documents are not yet in place. So the spent nuclear fuel characterization problem cannot be completely defined. That presents a challenge to this project. In the short term, it will be most fruitful to consider SNF characterization problems that are presently facing DOE laboratories and lend themselves to the type of research specified in the core capabilities program.

An expert systems approach was evaluated for automated technical review of waste assay data. This approach to data validation for nuclear waste assays by an active/passive neutron instrument resulted in good agreement with nuclear waste experts performing the same task. The approach is gathering favorable interest from the TRU waste characterization program at INEEL. Continuation of this effort will lead to new applications of expert systems and intelligent processing within the SNF characterization arena.

The use of neural networks for inversion of eddy current data was investigated and found to have the potential to predict the thickness of a metal sample over a range of sample thicknesses and under the influence of mechanical liftoff.

For the task on imaging in constrained environments, a laboratory system has been used to begin the process of correcting for geometric alignment errors in 3D imaging. Several data sets have been collected to test theories on geometric alignments. Also, collaboration has begun with the Medical Imaging Research Laboratory at the University of Utah for development of 3D imaging theory and reconstruction algorithms.

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NONDESTRUCTIVE ASSAY

Y. D. Harker

Scope and Objective

Nondestructive assay (NDA) has long been a major part of the INEEL core technologies. As a result of a strong commitment to fundamental nuclear and neutron physics research coupled with a strong application effort, this laboratory has established an international reputation in fundamental and applied gamma ray spectrometry and neutron-based assay methods. This NDA research project is to build on the existing technology base and perform research related to radio-assay signatures for elemental identification and quantification.

Technical Accomplishments

Background

The priorities for this project have been established by:

- Assessing current and future needs for NDA at the INEEL and the DOE complex
- Assessing the state of the art and what is being developed at other government laboratories, universities, and in the private sector
- Keying on those areas where the INEEL can make a positive contribution to the overall enhancement of NDA.

Because of the INEEL's extensive involvement in environmental issues—such as transuranic waste characterization, site characterization and remediation, and spent nuclear fuel characterization and storage—the leaders and team members of this NDA research project have firsthand knowledge and experience related to NDA issues that face the INEEL and the DOE complex. Therefore, the overall focus of this research is strongly influenced by the experience gained at the INEEL and our perspective of present and future NDA needs related to environmental management.

With respect to the INEEL, the primary focus would be to perform research to aide development of advanced systems for actinide, fission product, activation product identification and quantification. Other areas where the INEEL NDA research can play a vital role are explosive and chemical agent identification/quantification, contraband identification, and industrial and mining process control.

All NDA methods require measuring signals produced by the assay object, caused by either natural or induced activities. A successful NDA method has a measured signal that uniquely identifies the element or compound in question. This signal can be analyzed to produce an accurate estimate of the absolute strength of the source activity. Nuclear methods, in particular those involving gamma ray and neutron emission, are commonly used in NDA because the emitted radiation can penetrate through considerable amounts of material and the signature can uniquely identify the element.

Since the early days of atomic energy research, nuclear-based NDA methods have increased their capabilities in terms of providing more information and also improved accuracy. However, the NDA methods commonly used today continue to rely on singles counting gamma spectrometry and singles and simple coincidence neutron counting methods using ^{3}He neutron detectors. These techniques were developed over 20 years ago. Since then, advances in technology have been in better and faster acquisition methods and analysis routines. One focus of this research project is to take advantage of the massive revolution in computer-based acquisition systems and in the development of large high-resolution gamma detector/spectrometers. It is also focused on utilizing advanced counting methods developed in recent nuclear physics research such as large nuclear detector array and multi-parameter spectral analysis of coincidence events. When assaying for fissile material, for example, these advanced methods provide a means to uniquely identify the fission fragment nuclides at each fission event and thereby uniquely identify the fissioning nuclide. During this past year, a measurement effort was started to measure multiple gamma ray spectra correlated with fission events (i.e., correlated within 10^{-22} seconds). The primary purpose of the current experiment is to develop the database needed by future fissile assay systems operating on the correlated fission fragment detection method. A secondary purpose of these measurements is to provide additional data to understand the nuclear dynamics of fission during and immediately following the event. At this time, correlated fission fragment spectral data are being accumulated for neutron-induced fission of U-235, a primary fissile material in spent nuclear fuel and in nuclear waste. Similar data will be measured for Pu-239 and other actinides in the future. The direct fission fragment gamma radiation has, in general, higher energy components, which are more penetrating through matter than lower energy components. The more penetrating the radiation means that there will be less signal attenuation. In principal, the smaller the correction for signal attenuation is, the more accurate assay result is. This can have a profound effect on the accuracy of nuclear waste and spent nuclear fuel characterization.

While new signatures and the assay methods are the long-term goals of this NDA research project, there are also short-term goals to improve the nuclear database used by current NDA methods and to develop improved analysis methods to support current applications. During this past year, improved measurements of low-energy gamma ray spectra of the actinides were initiated. Since the current gamma-based assay systems rely almost exclusively on low-energy gamma rays in their analysis, these measurements have a direct impact on the quality of assay data involved in characterizing transuranic waste and spent nuclear fuel.

In the area of improving analysis methods for current gamma ray-based NDA applications, there has been a multi-faceted effort to understand in detail gamma ray transport from point of origin to point of detection. Since low-energy gamma radiation is used in their analysis, understanding the details of gamma transport is critical to improving the accuracy of current assay systems. The applications under study range from predicting the intrinsic response of the germanium gamma ray detector itself to predicting the response of germanium and other gamma detectors in complex “real geometry models” such as large transuranic waste containers and field applications involving prompt gamma neutron activation analysis. Understanding the intrinsic response of detectors is not only key to understanding NDA transport problems, it is also critical to certain aspects related to nuclear structure research.

FY 1998 Accomplishments

Actinide Signature Measurements

The focus in the actinide signature measurements area centers around a series of experiments ongoing at the Argonne National Laboratory (ANL-E) Intense Pulsed Neutron Source (IPNS). These measurements are designed to determine the prompt fission fragment isotopic yields produced during neutron-induced fission. During this past year, the measurements have focused on neutron-induced fission of U-235. Knowledge of these yields and their associated high-energy (1 MeV to 5 MeV) gamma ray signatures will be used in advanced NDA techniques utilizing correlated counting methods such as the spent nuclear fuel assay system being developed at the INEEL.

This work is a collaboration of the INEEL, ANL Physics and IPNS Divisions, and university participants. The ANL Physics division has provided 10 Compton-suppressed, high purity, germanium (HPGe) gamma ray detectors for this experiment. ANL IPNS has provided the neutron beam time essentially free. University participants will utilize the resulting data to study the basic physics of fission and the nature of the fission fragment isotopes at time of or immediately following the event. There is also an initiative to involve Russian scientists from Dubna laboratory.

For NDA, the coincidence method of this experiment can be used in an assay system to uniquely determine the fissioning nuclide via charge balance and mass balance of the fission fragments. An example of this process is shown in Figure 1. In this figure the decay schemes of fragments of Pu-240 spontaneous fission are shown. In this example the high mass fission fragment is Te-134, which is measured in coincidence with the low mass fragment which would be for Pu-240 spontaneous fission an isotope of molybdenum. The particular isotope of molybdenum would depend on the number of neutrons emitted during the fission. In order for this assay to work, it will be necessary to develop a database of prompt fission fragment gamma ray spectra for each fissile nuclide expected in the material.

During this past year, the coincidence counting experiment was set up at IPNS. Data acquisition of prompt fission fragment, gamma ray spectra from neutron-induced fission of U-235 commenced in June 1998 is currently in progress and will continue to about the end of October 1998. The goal is achieve data from 10^8 to 10^9 fissions. Figure 2 shows the experimental setup at IPNS and Figure 3 shows the data acquisition system. The key advancement in these measurements is that the data are acquired in “list mode” (i.e., on an event-by-event basis). Because the data are acquired on an event-by-event basis, they can be analyzed in any number of ways via changes in the analysis software. For example, the coincidence analysis time window can be altered by a software parameter change rather than requiring a whole new set of data to be taken.

Figure 4 shows an example of a gamma ray spectrum taken in this experiment. It is particularly worth noting the number of high energy (>1 MeV) gamma lines exhibited in this spectrum. In normal gamma ray spectral analysis, the major lines used for analysis have energies less than 500 keV. The high energy gamma lines will be extremely useful in quantifying the fissile material because they have high penetrability and therefore the signal will not be attenuated as much as would be the case for lower energy gamma rays.

Nuclear Data Measurement and Evaluations

Actinide Low-Energy Gamma Ray Spectrometry Measurements. Since the development of the primary database[a] used in gamma spectrometry NDA systems, there have been major improvements in germanium detector technology leading to better resolution and sensitivity. The new detectors are used in the state-of-the-art NDA systems, but the database used in the analysis was developed using older, lower resolution detectors. Consequently, much of the spectral details currently observed with the new detectors is missing in the database. The primary objective in this activity is to improve the γ-ray spectral database so that it matches the resolution of current detector technology. The second objective is to clean up the database gamma ray spectra by eliminating the artifacts of measurement that are not part of the nuclide decay, such as x-rays produced by the detector shield environment. Since many gamma-based NDA systems use low-energy to assay for actinides, the initial focus is on measuring low-energy γ-ray spectra for several actinide nuclides.

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[a] The use of database in this context is generic and does not refer to any particular database such as the INEEL Gamma Ray Spectrum Catalogue. It simply refers to the general status of nuclear data used in analysis of NDA data.

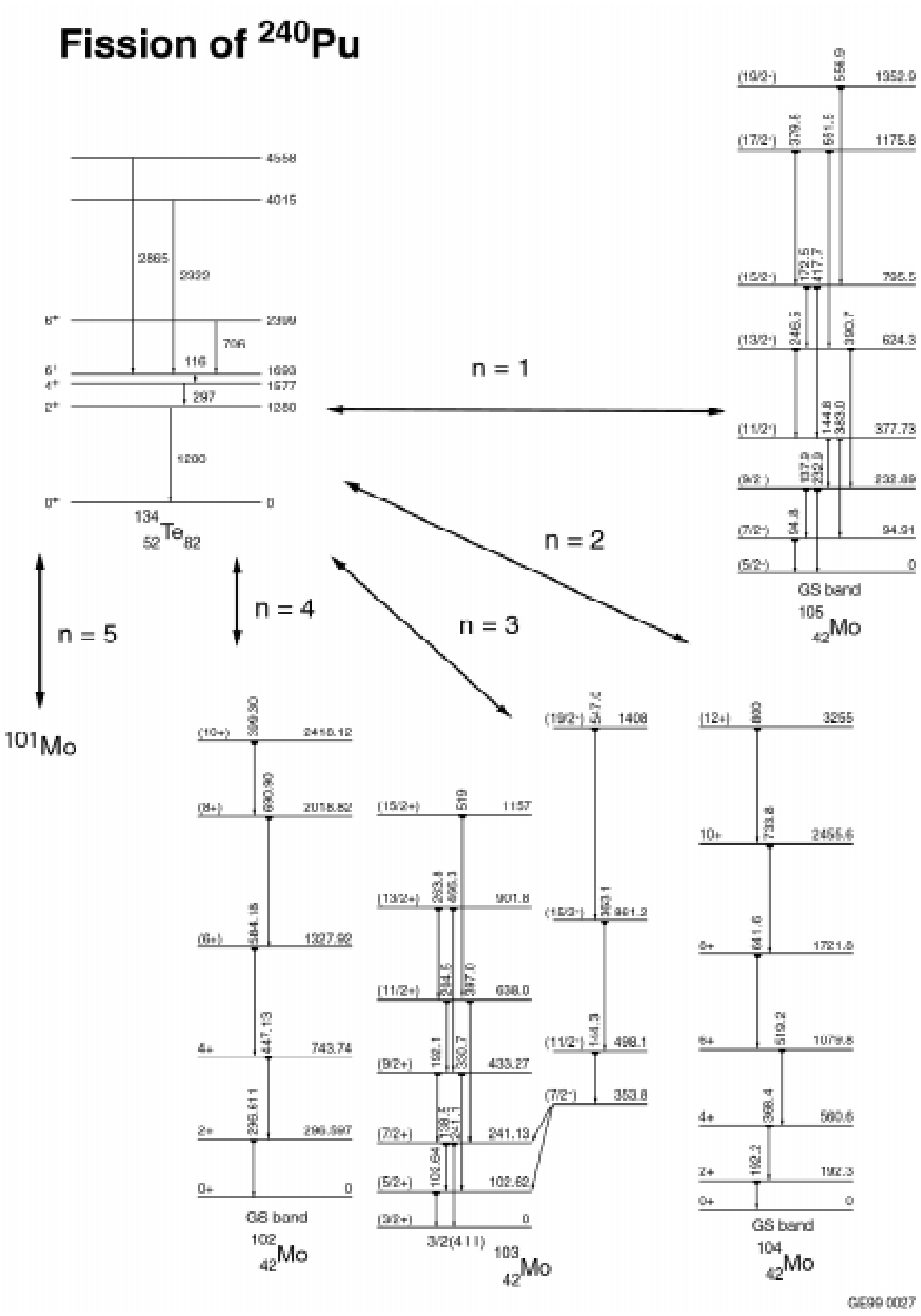

Figure 1. Fission of Pu-240 where Te-134 is measured in coincidence with the isotopes of molybdenum.

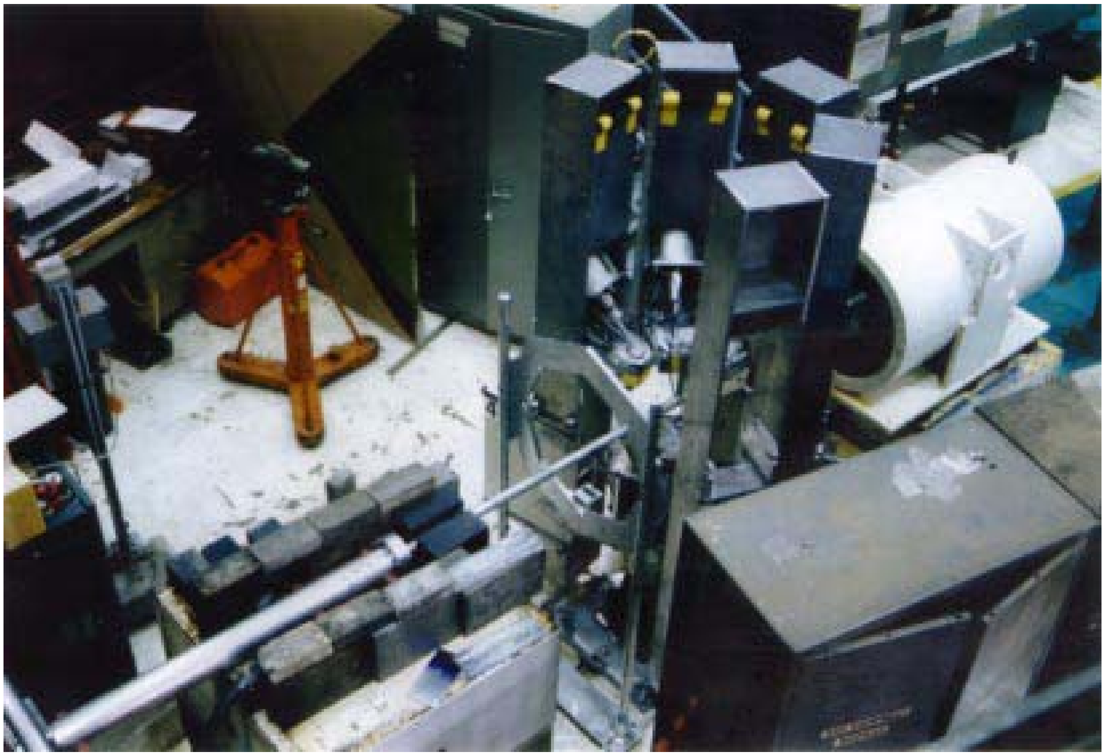

Figure 2. Experimental setup at IPNS. The neutron beam line comes for the lower left corner. The detector array is in the center right of the picture. At the center of this array is the uranium target. The white cylinder at the right of the picture is the neutron beam stop.

Figure 3. Data acquisition system at IPNS.

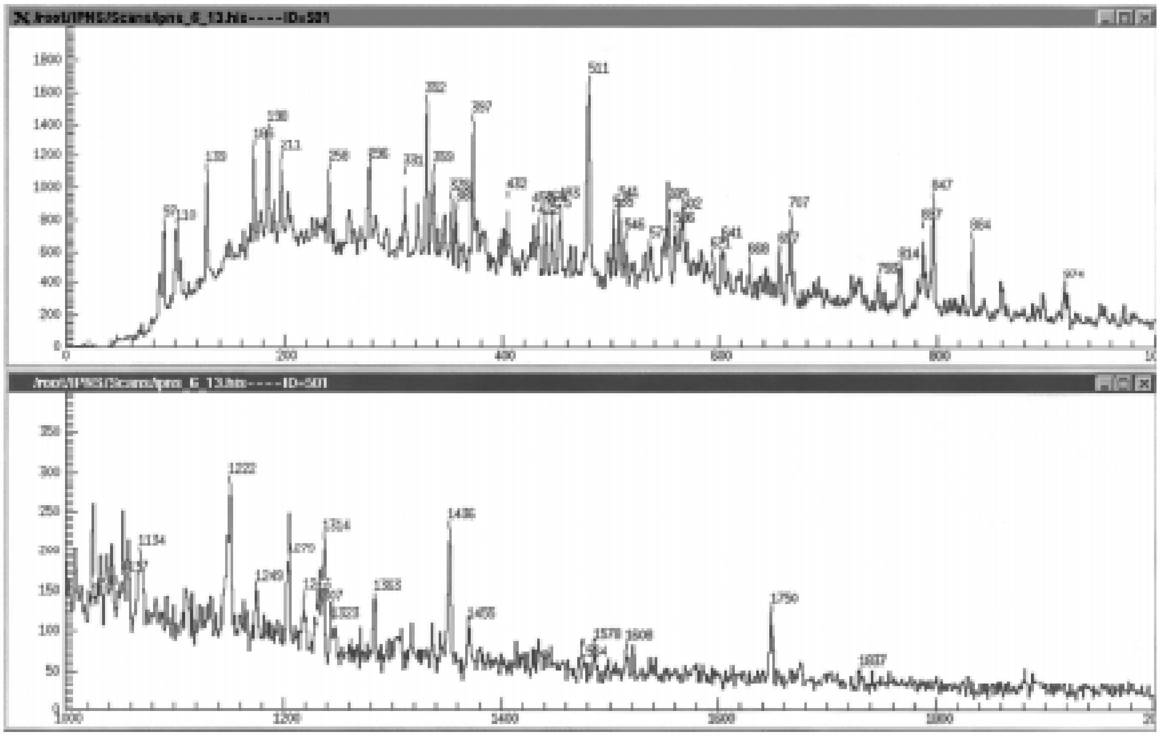

Figure 4. Preliminary gamma ray spectrum taken by the IPNS experiment. The spectrum comes from fission fragment analysis of neutron-induced fission of U-235. The x-axis is the channel number, which is proportional to the gamma ray energy. The numbers at the tops of the more prominent peaks in the spectrum indicate gamma ray energies (in keV) associated with the corresponding peaks.

In order to carry out high-quality γ-ray spectral measurements, a new Ge detector shield was constructed in a radiation physics laboratory at the INEEL Test Reactor Area (TRA). The primary shield material is lead, which eliminates spectral contamination from outside sources. The lead enclosure is lined with layers of cadmium, copper, and aluminum. The liners were added to eliminate low-energy x-ray contamination so that gamma ray spectra are valid down to 10 keV.

Gamma ray spectra, over the energy range from 10 keV to 1500 keV, have been acquired for ^{233}U, ^{238}Pu, ^{239}Pu, ^{210}Pu, ^{242}Pu, and ^{241}Am. These spectra are high quality and will be made available for the INEEL and others to update their databases. Because much of the transuranic waste at the INEEL and other DOE sites has been stored for over two decades, there is considerable interest in gamma ray spectra from "aged" samples of actinides. "Aged" sources often include significant amounts of the radioactive daughter activity. For example, a gamma ray spectrum of a ^{233}U sample that had aged over 20 years exhibited a prominent line at 440 keV from the decay daughter ^{213}Bi. The 440 keV line has already been used at the INEEL Stored Waste Examination Pilot Plant (SWEPP) to corroborate the presence of small amounts of ^{233}U in some containers of transuranic waste.

One of the databases where the new gamma ray spectrum data will appear is the INEEL Gamma Spectrum Catalogue. Under another program, this catalogue is being updated and produced on compact disk. Figure 5 is a sample page from the new Gamma Spectrum Catalogue. In this example, one can see that all the most commonly used decay information is immediately available.

A paper related to actinide spectral measurements will be presented at the Nondestructive Assay Waste Characterization Conference in November 1998 in Salt Lake City. Presentations in memory of

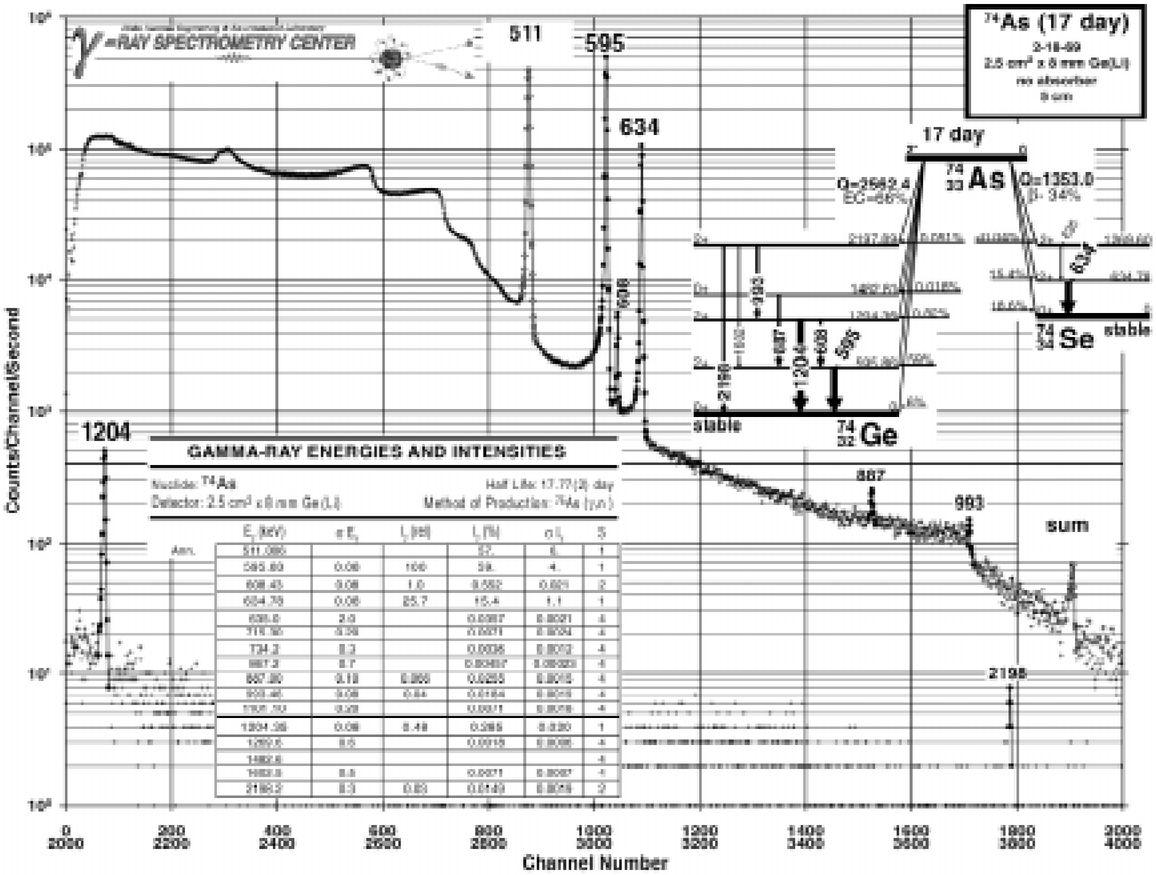

Figure 5. Sample page from the Gamma Spectrum Catalogue.

R. L. Heath are planned for the November meeting of the American Nuclear Society and are entitled "Russ Remembered" and "An Electronics/CD-ROM Version of the Gamma Ray Spectrum Catalogue."

Nuclear Structure Research. Actinide gamma ray spectrum measurements discussed above are part of a larger effort in nuclear measurements and nuclear structure research. Beginning in July1998, the scope of the nuclear measurements under the NDA project was expanded to lay the foundation for formation of a nuclear structure research program at the INEEL. Nuclear structure research at the INEEL has been in the past, and is expected to be in the future, the springboard to our leadership in nuclear metrology and to developing new applications of applied radiation measurements (e.g., the gamma spectral measurements used in NDA).[b] The objectives of the nuclear research initiative are:

- Enlarge the scope of gamma ray spectrum measurements to include more than the actinide spectrum measurements, currently in progress. The priorities will be established by reviewing the current databases and finding where there are holes in the data. For example, the gamma data from neutron inelastic scattering is sorely lacking and yet this reaction is

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b. Nuclear structure research and NDA research, supported by the Core Competency Program, fall under the technical envelope of the INEEL Gamma Ray Spectrometry Center. This center brings together many activities (funded by different sources) with the common goal to promote basic and applied nuclear science at the INEEL. Because this laboratory has long been recognized for its leadership role in gamma ray spectrometry, that term is used in the name of the center. However, the technical scope of the center is not limited to just gamma ray spectrometry but involves all basic and applied radiation science.

often used in prompt gamma neutron activation analysis. Studying the decay of the inelastic scattering products will lead to updated decay scheme information to be used as a part of nuclear structure research.

- The INEEL will have to look to other laboratories to produce the unique source materials needed for these studies, to perform some of the measurements and/or to provide facilities where in situ measurements can be done. Therefore, one of the initial goals of this effort is to establish contacts with other laboratories, which have one or more of the following:
    - Capabilities to produce the required source materials
    - Capabilities to perform radiochemical separations
    - Capabilities to collect high-quality spectral data
    - Facilities with which to measure prompt gamma ray spectra produced by neutron capture or neutron inelastic scattering.
- One of the goals of this research is to develop a long-term technical resource in nuclear research in terms of facilities and expertise. In this context, contacts with universities that have nuclear engineering or applied radiation schools have been made to identify potential candidates for staff positions under this program at the INEEL.

The following are the technical accomplishments made in FY 1998 relative to these objectives:

- Contacts were established with the University of Michigan, University of Washington, and Oregon State University. The three universities were visited by the INEEL personnel who made preliminary evaluations of their capabilities to produce radionuclides, perform radiochemical separations, and collect high-quality gamma ray spectral data. It was determined that the University of Michigan and University of Washington have radiochemical separation capabilities useful to this research. Oregon State University has a very good irradiation facility that can be used to produce radioactive sources and facilities that the INEEL personnel can use to perform radiochemical separations and gamma ray spectrum measurements. University of Michigan has good gamma ray spectral measurement capabilities. The University of Michigan staff will prepare a proposal to carry out work to support the INEEL research involving: (1) radiochemical separation of actinide daughters and measurement of their gamma ray spectra, and (2) production of radioactive samples in their reactor, Oregon State University will prepare cost estimates for irradiations and for support to the INEEL personnel as soon as we identify the isotopes of interest.
- The Los Alamos Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory (LANL) was visited by the INEEL personnel. The possibility of using LANSCE for irradiations was discussed together with the feasibility of using their existing measured data to begin the development of a spectral database for the interaction of fast neutrons (i.e., >1 MeV) with various elements. Agreement to use their data was obtained.
- Four Universities (Michigan, Washington State, Oregon State, and North Carolina State) were visited in an attempt to identify potential candidates for staff positions at the INEEL. It is anticipated that during FY 1999, two new members will be added to Radiation Physics staff to support this and other research—one with expertise in gamma ray spectrometry and one with expertise in calculational methodologies related to gamma ray spectrum analysis

simulation of gamma ray spectra. Several potential candidates were identified at the universities visited.

Nondestructive Assay Data Analysis Methods Development

Two critical elements affecting accuracy of converting a detected signal to an absolute assay result are:

- Quantification of signal attenuation
- Quantification of the intrinsic response of the detector.

Four issues, related to signal attenuation and detector response, are being studied in this project:

- Precise calculation of the intrinsic response of a high purity germanium detector
- Gamma signal attenuation when assaying large volume containers
- Calibration of in-field gamma ray detectors for prompt gamma neutron activation.
- Automated routine for determining uranium enrichment.

Precise Germanium Detector Efficiency Study. The objective of this study was to explore the possibility of determining via simulation the relative γ-ray efficiency with an uncertainty of ~0.1%, which is significantly better than the common uncertainty of ~5.0%. While efficiencies with an uncertainty ~5.0% are adequate for most NDA applications, the higher level of precision is needed to more accurately identify the nuclear decay characteristics associated with nuclear decay scheme development.

In this study, we have made calculations of the efficiency with a Monte-Carlo electron and photon transport code using a model of a detector at the University of Michigan on which precise efficiency measurements have been made over the limited energy range of 662 keV to 1,332 keV.

Measurements were made for four radionuclides each of which has a pair of γ-rays with essentially equal intensities which allows one to measure the relative efficiency very accurately. The Monte Carlo results agree with these measured efficiency ratios to about 0.1%. The Michigan group developed an interpolation scheme to provide the efficiency at all intermediate γ-ray energies. Comparisons of these values with those from the Monte Carlo code, indicate that it may be possible to generate efficiency values with an uncertainty as small as 0.1%.

The precise efficiency work has involved a collaboration with Professor Martin Ludington, Albion University, Albion, Michigan; Professor Ron Lleming, University of Michigan; and Dr. Ayman Hawari, formerly of the University of Michigan and University of Texas.

Gamma Detector Response Involving Large Volume Containers. A common geometry in waste assay involves a large container (typically a 55-gallon drum) with one or more detectors located adjacent to it. In addition to geometry effects, assay of large volumes introduces a very significant bias due to attenuation of the gamma rays by the matrix medium. Segmented gamma scanners and similar devices attempt to measure this attenuation by using external transmission sources and measuring the transmission across the container. From the transmission measurement an attenuation correction is made to the measured signal. This correction assumes that the source is uniform across the path length of the transmission correction. Recent tests at the INEEL and simulation experiments at the University of Florida have shown that transmission-based assay systems are able to provide reasonably accurate estimates of the total source activity in a 55-gallon drum so long as the density of the matrix was ~0.4 g/cc or less. On the other hand, assay systems have been developed which use computed tomographic (CT) reconstruction to determine the source strength. The CT methods have shown great promise but generally require very long assay times and the small improvement in accuracy will not support the increased assay times for most applications.

Given the situation with existing assay systems, it was decided to consider if there are ways to improve the accuracy of simple passive gamma-based waste assay systems by making better use of the raw data already produced by those systems.

For this study the SWEPP Gamma Ray System (SGRS) was chosen. This system is basically a Canberra Q-2 passive gamma assay system. It consists of a 15 cm thick steel enclosure that surrounds a 55-gallon drum. Multiple HPGe detectors (in SGRS there are up to four) are situated in a vertical stack looking at the side of the drum through circular penetrations in the shield. During assay, the drum is rotated and a gamma ray spectrum is acquired by each of the detectors. After the acquisition is complete, the individual detector gamma ray spectra are summed to produce a composition spectrum. The composite spectrum is analyzed to yield total source activities in the drum. In the standard SGRS analysis, attenuation is accounted for by using simple exponential corrections and assuming that the source is planar and that the gamma rays are being attenuated through a slab of matrix. Given the uncertainty concerning the accuracy of this attenuation correction, the SGRS is not currently used to provide absolute assays but is used only to provide activity (or mass) ratios. Absolute activities (masses) are then derived by combining the SGRS mass ratios with absolute measurements of plutonium and/or uranium using a neutron-based assay system. The SWEPP process has proven to be quite successful in assaying a large spectrum of drums with varying densities and contents; however, it does require two instruments. It is expected that if a good correction for gamma attenuation can be applied, then a gamma-based assay alone should be capable of providing adequate absolute assay results. Therefore, the goal of this study was to examine the capabilities of such a system in obtaining absolute assay data.

Because of the amount of assay data available from SWEPP and from destructive radiochemistry analysis of drums stored at SWEPP, the matrix material chosen in the initial studies was solidified aqueous waste (also known as inorganic sludge). This waste form has both an advantage and disadvantage. Its disadvantage is that its density is comparatively high; thus the attenuation of the gamma signal will be large. Its advantage is that from process knowledge the source distribution will be reasonably uniform, which offsets the severe attenuation problem.

The initial approach in this study was to perform a detailed gamma ray transport calculation using a Monte-Carlo N Particle (MCNP) code. The objective here is to take the results from the detailed MCNP calculation and study gamma attenuation/detector response under these circumstances. In the long-term, MCNP transport calculations will be replaced by deterministic transport calculations which do not have the detail of the MCNP calculation but will run faster. The objective here is to have a routine that is fast enough to analyze the results and to produce attenuation corrections in real time.

The MCNP code was developed at the Los Alamos National Laboratory. It is able to track histories of neutrons, gamma rays and charged particles. This code is very flexible and lets one set very complex geometry/material models. For this study, the geometry of the drum, contents, shield and detectors were modeled in great detail. The end of result of this calculation is a matrix-attenuated efficiency curve versus gamma ray energy for each detector. As explained above, the individual SGRS gamma ray spectrum data are combined into a composite spectrum. To compare with SGRS measured data, the individual detector-calculated efficiency curves are combined to produce a comparable composite efficiency curve. Figure 6 shows the MCNP-generated efficiency curves for the SGRS and a matrix of solidified aqueous waste. In this figure two efficiency curves are displayed. The 3 detector average curve corresponds to the average detector response if only the three bottom detectors are used in the assay. The 4 detector average curve corresponds to the average detector response if all four detectors are used in the assay. The reason for having both curves is that there were times when only the bottom three detectors were operational at SWEPP. Average detector efficiency curves (rather than summed) are used because of the way the individual detector spectra are combined in the SGRS gamma spectrum analysis.

One of the quality checks on the operation of the SGRS is to compare the mass ratio of direct value of the U-235 to Pu-239 mass ratio with the indirect value of the U-235 to Pu-239 mass ratio. The direct value is determined from gamma lines of U-235 and Pu-239. The indirect method mass ratio is determined in a two step process where the intermediate step is to determine the Am-241 to U-235 mass ratio and the Am-241 to Pu-239 mass ratio. The indirect U-235 to Pu-239 mass ratio is then determined by dividing the latter mass ratio by the former. Since the direct and indirect methods use different gamma ray lines, agreement between the two ratios indicate that the assay is internally consistent. This check was performed on over 400 drums of solidified aqueous waste. Three analysis scenarios were compared:

- Standard SGRS gamma analysis package with empty drum efficiency curves
- Standard SGRS gamma analysis package with the MCNP efficiency curves
- Modified SGRS gamma analysis where the absolute activities (masses) are estimated using the MCNP efficiencies and the mass ratios determined from the absolute values.

The results are given in Table 1. In this table, a failure means that the difference between the direct and indirect mass ratio is greater than twice the combined uncertainty. Based on this criterion, a 5%

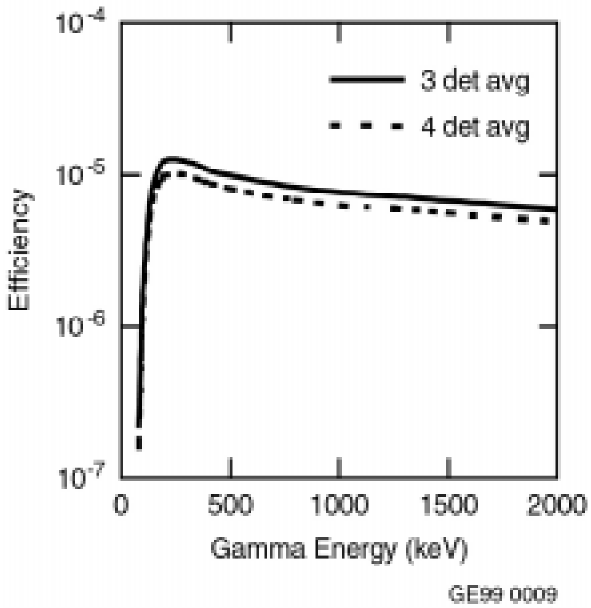

Figure 6. MCNP calculated efficiency curve for the SWEPP gamma ray system assaying solidified aqueous waste (density = 1.3 g/cc).

Table 1. Data quality check (direct vs. indirect U-235 to Pu-239 mass ratio).

Analysis Scenario	Percent Failures
SGRS Standard Analysis	8%
SGRS Std. Analysis (modified with MCNP efficiency)	5%
Mass ratios determined from absolute activities using MCNP efficiency.	0%

failure rate is considered statistically satisfactory. The 0% failures for the third scenario is somewhat misleading in that the calculated uncertainty is probably too large. This is because the error propagation did not take into account correlated parameters. However, examination of the third scenario direct versus indirect ratios indicates that they agree to within three significant figures. As can be seen from these results, the use of the MCNP efficiency is an improvement over the standard approach.

A paper discussing the use of the matrix-attenuated efficiency data has been submitted to the Sixth Nondestructive Assay Waste Characterization Conference to be held November 17–19,1998, in Salt Lake City.

Because of the immediate success achieved, the SGRS gamma spectrum analysis code has been modified by the SWEPP support group (at their expense) to use efficiency data generated from this study. The new analysis routine uses the matrix-attenuated efficiency data to calculate directly the absolute activity values and ratios. At this time, the absolute analysis is run in parallel with the standard ratio analysis on every drum assayed at SWEPP. As a result, we get a running tally on how well our efficiency data works when assaying a large population of real waste drums. The modified analysis results are also used by the SWEPP data reviewer to independently check the results of the standard analysis. Having data from real waste drum assays is a definite benefit to our study. In addition to including the parallel analysis routine in their software, SWEPP operations support have also included the option to use matrix attenuated efficiency data to enhance the quality of their standard ratio analysis.

As indicated above, using MCNP to calculate matrix-attenuated efficiency data is only the first step in this study. It is planned to examine methods to generate matrix attenuation correction routines that operate in real time on individual drum assays. Professor Samim Anghaie from the University of Florida who has developed prototype source reconstruction algorithms has been contracted to assist in developing such algorithms for this application. It is expected that at least one advanced degree research thesis will be generated by this study.

Calibration of In-Field PGNAA Instruments. The goal of this task is to develop an analytical method for calibration of instruments used in prompt gamma neutron activation analysis (PGNAA). In order to realize this goal, an analytical method to calculate PGNAA spectra is needed together with a method to analyze the very complex PGNAA spectra. In pursuit of this goal, the FY 1998 objectives are:

- Investigate North Carolina State University's Monte Carlo computer program. This is to be done by modifying the program to accommodate geometries used by PGNAA, bring these programs to the INEEL, learn how to use them, and begin to use them to calculate spectra for cases where measured data can be obtained.

- Collect PGNAA spectra from materials of interest and use these spectra to evaluate gamma ray analysis programs and North Carolina State University's Monte Carlo program.

A collaborative agreement and subcontract with North Carolina State University (NCSU) has been established. Under this collaboration NCSU has modified their CEARPGA program to accommodate three PGNAA geometries: 1-gallon paint can with axis parallel to detector axis, 1-gallon paint can with axis perpendicular to detector axis, large planar sample geometry. The modified CEARPGA program has now been given to the INEEL for testing.

PGNAA spectra for use in evaluation of the CEARPGA program were obtained from materials of interest (e.g., phosphate ore). These spectra were also used to evaluate the capabilities of the commercially available gamma ray spectrum analysis programs OMNIGAM and GammaVision. OMNIGAM was found to be totally inadequate for PGNAA use. It had difficulty in finding and analyzing some of the smaller capture gamma ray peaks of interest (i.e., it missed some peaks, and it got the wrong answer for other peaks). GammaVision proved to a better program for PGNAA purposes, but it, too, had problems. For example, the automatic mode generally overestimates (sometimes by as much as a factor of 2) the areas of small peaks on a relatively constant background, although the manual mode (which involves operator interaction and judgment) gives good results. For peaks on a varying background, both modes seem to under-estimate (sometimes by more than 20%) peak areas. PC-GAP, developed by the INEEL, proved to be the best program for PGNAA spectra (although it, too, requires operator interaction). Peak areas calculated by PC-GAP were comparable to results obtained by hand analysis by an experienced gamma ray spectrometrist.

Automatic Portable Uranium Assay System. Figure 7 shows an automatic portable assay system that is being developed to determine the enrichment of uranium inside a container. It is capable of assaying bulk uranium samples surrounded by different kinds of unknown shielding materials. The system is geometry independent and requires no absolute efficiency calibrations. The system supports several applications such as monitoring and assaying of mixed and metallic spent fuels and special nuclear materials.

The technique uses the intensity ratio of 186-keV gamma ray from U-235 to the 1,001-keV gamma ray from U-238 to determine enrichment. This is done by making the necessary corrections including gamma ray attenuation in a uranium sample (self-attenuation), in shielding materials and in the container using an Eu-152 source. The results are compared to the theoretical curve in Figure 8 to deduce the isotopic ratio.

Figure 7. Automatic portable uranium assay system.

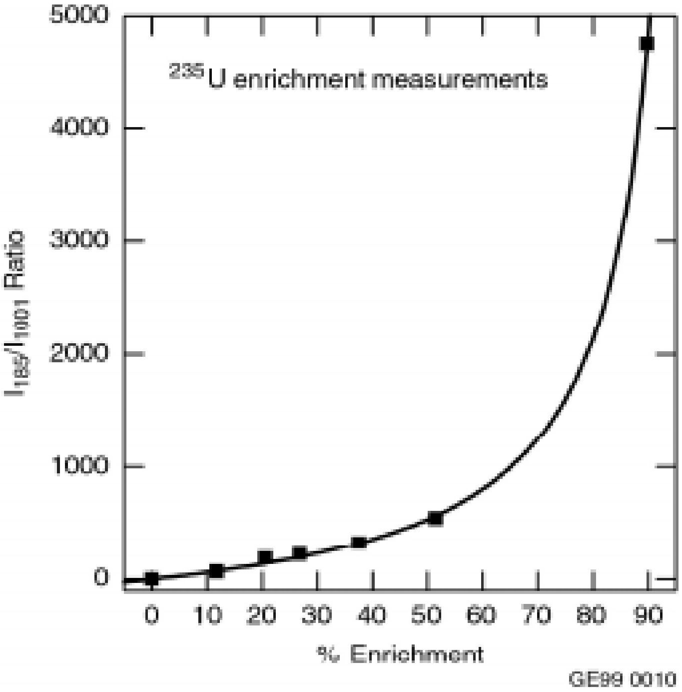

Figure 8. Theoretical plot of $I_{185}/I_{1,001}$ versus enrichment.

Self-attenuation of gamma rays in high-Z uranium at first seemed to be disadvantageous, but quite to the contrary it turned out to be a very useful piece of information in determining the exact location of a uranium sample in the container.

Preliminary measurements were performed to determine the enrichment of unknown uranium samples (ranging from depleted uranium to 90% enriched) placed in different barrels at random locations. The following table shows the results of our successful tests.

Sample #	Measured Location From the Bottom	Measured Enrichment	Actual Enrichment
1	17”	54%	51.8%
2	9.5”	29%	27%
3	12”	40%	37.7%

The technique was very successful in determining not only the exact location of the HEU samples in the containers, but also to determine their enrichments to within 2%.

Also, the results of tests performed last year on Advanced Reactivity Measurement Facility (ARMF) spent fuels (for both bare fuel and fuel inside 55-gallon drums) were successful and encouraging. The results are summarized in the following table.

Method	Bare Fuel	Fuel in Barrel
Singles	76% ± 16%	70% ± 20 %
Coincidence	80% ± 12%	86% ± 20 %

At this time, the main task for uranium enrichment is to develop necessary software and hardware to make the system fully automatic. By the end of FY 1998, the following actions will have been taken or completed. It is expected that an operating fully automatic assay prototype will be completed during the first quarter of FY 1999.

- Several options for interfacing hardware and software were investigated.
- ORTEC "Gamma Vision" data acquisition system was selected because of its simple interface with the existing hardware and easy integration with software.
- 80% of steps needed for different measurements and automation control is finished.
- 40% of the software required for analyzing, interpreting the spectra, and deducing the enrichment is completed.

NDA Summary

Since this project commenced in February 1998, great progress has been made relative to NDA research. A major emphasis is on basic research related to developing new signatures that can uniquely identify fissile nuclides. Other areas of interest are accumulation and evaluation of nuclear data needed to support existing NDA methods and improving analysis methods to support existing gamma-based NDA methods. In the last area, four separate but related efforts are in progress. They are (a) developing an analytical method to determine the intrinsic efficiency of a germanium gamma detector to an accuracy of 0.1%, (b) developing gamma-signal attenuation algorithms for real waste assay systems, (c) calibrating in-field gamma detectors used in prompt gamma neutron activation analysis, and (d) developing an automated uranium enrichment analysis.

With respect to new actinide fission signature measurements, a major experiment has been initiated at the Argonne National Laboratory Intense Pulsed Neutron Source. Not only will this experiment generate data for use in developing new fissile assay systems, it will generate basic nuclear data that researchers can use to understand the physics of fission and the nuclear structure of highly deformed nuclei. At this time, correlated fission fragment spectral data measurements for neutron-induced fission of U-235 are in progress and will continue through the end of October 1998. Preliminary reviews of the data indicate that the quality is exceeding expectations. Following the end of the U-235 data run, analysis of volumes of correlated spectral data will commence. The next reaction to be studied will be neutron-induced fission of Pu-239. That data accumulation will begin about the first of calendar year 1999 and is expected to continue through July or August of 1999. The next nuclide to be studied will depend on finding a suitable sample.

In the area of nuclear data measurements, a new laboratory for precise gamma spectrometry measurements has been set up at the INEEL Test Reactor Area. Measurements of high-resolution gamma ray spectra for several actinides have been completed. The quality of the new data is superior to that from the past. In addition to spectrum measurements using purified sources, this program has measured gamma ray spectra from "aged" sources where daughter activities are also measured. This turns out to be a very important resource when assaying transuranic waste that has been in storage for a long period of time. For example, spectral data from an "aged" U-233 sample was used to determine whether or not U-233 is present in transuranic waste drums assayed at the INEEL SWEPP facility.

The ground work for a nuclear structure research effort at the INEEL has been initiated. It is recognized that nuclear research at an application oriented laboratory where basic and applied research is conducted side-by-side is the key to the INEEL's success both as a premier nuclear metrology laboratory and as a developer of new applied techniques for NDA, etc. Several laboratories and universities have been visited to develop a national effort to produce high quality radioactive source materials and to perform advanced nuclear data measurements.

In the area of NDA gamma analysis methods development, much progress has been made in developing analytical methods to characterize detector responses under a variety of conditions. It has been demonstrated that under ideal laboratory conditions intrinsic detector efficiencies can be calculated to better than 0.1%. Accurate determination of detector efficiencies will greatly enhance the data analysis leading to nuclear decay schemes in nuclear structure research and will be the basis for understanding detector response for complex geometries.

The initial progress in understanding the details of detector response for assaying large waste containers has already produced results which, as a side benefit, improve the performance of the waste assay system at the Stored Waste Examination Pilot Plant. The goal in this study is to produce advanced signal attenuation correction algorithms for application on almost all gamma ray spectrometry-based assay systems. This work will be done in collaboration with the University of Florida.

The goal of developing an analytical method for calibration of instruments using prompt gamma neutron activation analysis is much closer to realization. In this effort, a contract with North Carolina State University has been initiated where their analytical code has been modified to accept more complex and application oriented geometries.

An automated portable uranium assay system is close to being implemented. The feasibility of the method was established by earlier work. The major focus of the current effort is to develop software and hardware that will perform the uranium analysis automatically.

Two papers on actinide gamma ray spectrum measurements and one paper on gamma-signal attenuation in large containers have been submitted for presentation at upcoming topical meetings.

ENVIRONMENTAL MODELING AND SIMULATION

L. E. Greenwade

Scope and Objectives

The Environmental Modeling and Simulation (EMS) task of the Core Capabilities and Technical Enhancement (CCTE) component has the charter to produce a robust, effective and modern set of computing technologies to support modeling and simulation of computational components of environment problems. The charter includes support for all elements of computational work including physical and process simulation, data analysis, and archiving along with appropriate visualization and communication tools.

The three principal tasks for FY 1998 involved were

1. Infrastructure development

2. Numerical optimization and data formats conversions

3. 3-D graphics.

Progress in FY 1998 was measured by four milestones concerned with developing an effective, integrated computing environment supporting environmental problems.

Technical Accomplishments

Infrastructure

During the past year, significant effort was made to build the Numerical Simulation Laboratory (NSL) into a usable, reliable, high performance-computing environment. The NSL team has worked on every aspect of the lab to meet this goal. Changes have touched everything from the name of the facility to the infrastructure underlying the operation of the lab. Team members have made improvements in the environment, hardware, networking, and software with the goal of building a state-of-the-art computing environment. This effort has been successful within the limitations imposed by the resources available. This section discusses improvements that have been made at the Numerical Simulation Laboratory and how these improvements work to create a usable, reliable computing laboratory. Briefly, the following areas will be discussed: name change, infrastructure, hardware improvement, network/system integration, user support and training, and the physical layout of the NSL.

This year marked a change of name from *Visualization Laboratory to Numerical Simulation Laboratory* (NSL). This was done in order to provide a better description of the facility's focus and capabilities. The NSL supports not only visualization, but many other areas of computing in the numerical solution to environmental problems. Users of the NSL facilities include computational chemists, physicists, systems engineers, Y2K analysts, immersive environment developers, 3-D modelers, and summer interns. The name *Numerical Simulations Laboratory* more accurately describes the focus of this facility.

Two major changes occurred in the computing infrastructure within the NSL—a migration from NIS to NIS+ and a move to a dedicated subnet. Both of these have resulted in dramatic improvements in the NSL team's ability to do system administration and to provide high levels of performance, stability, and integration while minimally impacting resources.

NIS+ is a replacement for Network Information Services (NIS). NIS is currently used on a sitewide basis at the INEEL to distribute system administration data to workstations. NIS suffers from a number of design limitations, including poor stability, minimal security, slow information propagation, nondistributed administration, and dependencies on network topology. NIS+ is designed to overcome the weaknesses of NIS, and to be scalable on large distributed networks. Some of the advantages of NIS+ over NIS are the greatly increased data security and integrity, rapid and efficient data propagation, and flexibility of distributed administration.

NIS+ is essentially a namespace, i.e., network database, to support efficient administration of workstations. This namespace contains system information for hosts and users that are then overlaid on the current computer network. It is important to note that the structure of the namespace does not depend on the underlying network. Inclusion in a specific NIS+ domain is an administrative concept rather than a requirement or condition of the network. NIS+ domains can then be grouped logically, rather than physically. This greatly increases the number of potentially geographically distributed workstations that may be administered effectively.

In the NSL implementation, we have created a domain nsl.inel.gov that is a subdomain of the inel.gov domain created and maintained by the IRM staff. The primary benefits for the NSL are: (1) the complete administrative control of the nsl.inel.gov namespace by NSL systems administrators, (2) the ability to make immediate alterations to network services to meet current needs, or to work around problems and (3) centralized administration of all user accounts and network information. The major disadvantages of NIS+ are the steep learning curve for administration and the often difficult migration from the initial NIS environment.

When changes were needed under NIS, several non-NSL people were required for the manual procedure for maintenance of network data. If a network information change was necessary, it required the coordinated effort of these people, usually requiring an exchange of multiple e-mails and phone calls. If any one person was absent, then the entire procedure was often delayed. To make matters worse, NIS updates require significant effort to be propagated through the networks—they are typically an overnight process. This situation resulted in 24–72 hour waits to complete changes, which often resulted in significant downtime for our systems. With NIS+, NSL team members can make changes and propagate them through the network almost instantly. When changes are final, we pass them to the INEEL NIS administrators for inclusion in sitewide databases.

Under NIS, it was necessary to maintain separate password files, host files, etc., on every machine in the NSL. This was a burdensome administrative task. With NIS+ this information is centrally administered, allowing for easy updates. This has the added benefits of reducing the time required to maintain the NSL computer systems and it supports a uniform interface for users. Although the initial configuration and migration to NIS+ is difficult, the advantages of central administration, stability, and rapid updates has made the effort more than worthwhile.

This year the NSL migrated away from utilizing one of the first floor east EROB subnets to a dedicated subnet within the NSL. This has had many positive impacts on both performance and administration. Advantages of the change include: (1) the ability to move or add machines without delay, (2) increased network bandwidth between NSL systems, (3) resulting network is easier to trouble shoot, and 4) it nicely complements NIS+. The only disadvantages were the time and cost to implement the new system, costs that have already been recovered by the reduced system downtime and decreased administration requirements.

With the dedicated subnet the only network traffic present is the traffic generated locally by NSL systems. Previously NSL not only had its own traffic but all the traffic of the east EROB 1 network. This made for a very crowded subnet, which impacted not only the performance of NSL systems but everybody else on the subnet. System problems due to network congestion were common. These problems have been eliminated by implementing the new subnet and overall performance has increased to approximately 20 times that previously available. The addition of the NSL subnet has supported the upgrade of NSL systems to use fast Ethernet rather than standard Ethernet. Speeds of network transactions have increased from 10 Mb/sec to 100 Mb/sec. This has substantially impacted performance of the systems and provides a growth path towards future networking technologies.

Prior to the implementation of the new NSL subnet, administrators for the NSL systems had to incur several delays when any changes needed to be made to the network. This frequently required a few days to happen. As the NSL is a working laboratory, changes are the norm rather than the exception. Changes were cumbersome for both NSL system administrators and INEEL network personnel. Now the NSL team has a block of IP addresses that may be used as needed and a switch where network connections can be changed as necessary. Coupled with NIS+, system administrators can make any changes to systems and network configuration without external intervention. Once changes are final, the information is forwarded to the correct people for inclusion in sitewide databases. This has cut the delay of introducing a new system to the NSL from days to a few minutes.

The NSL has made a number of hardware upgrades this year to increase the performance, capacity, and stability of the computing systems. The additions include:

- Five new workstations—three Sun Ultras and two SGI 02s. We replaced outdated hardware and provided increased performance and stability.

- New workgroup server—a Sun Enterprise 3500. This system is built to be fail proof with redundant CPUs, power supplies, IO boards, memory and hard drives. It serves the bulk of NSL applications, data, print serving, and users' home directories. Uninterrupted uptime is critical.

- 16 additional CPUs and 4 gigabytes additional memory for the SGI/Cray Origin 2000—expands total system resources to 24 CPUs and 6 gigabytes of memory. This greatly expanded the NSL's capacity for doing numerical- or graphics-intensive work.

- 2.2 terabyte digital tape library—using a special commercial file system, (SamFS) the NSL is able to provide the full 2.2 TB capacity of the tape library to users in a transparent fashion.

- Ceiling mounted projector—10 ft screen, seating for 12 people. This projector can be used to display videos, mirror the display of any NSL workstation, or mirror a visitor's laptop. The system is used frequently for demonstrations, group work sessions, and training.

- Networking hardware upgrades—the upgrades have greatly improved the performance, reliability, and maintainability of NSL systems.

- Accom digital video array—has been used extensively in the past year to effectively record animations produced on NSL workstations to high quality videotape. This system is directly accessible over the INEEL network so that it may function as a resource to any INEEL user with the need to produce videotape from a series of computer generated images and can be used to support technical and program reviews and numerous training applications.

- Additional memory and disk—was acquired for existing systems to better accommodate the steadily increasing problem sizes and complexity.

The net effect of these hardware upgrades has been increased performance, greater reliability, easier maintainability, and better accessibility for users.

A significant effort has been made in the past year to improve integration and usability of NSL equipment. The migration to NIS+ and the dedicated subnet allowed substantial progress to be made in the difficult task of integrating the large array of heterogeneous equipment contained within the NSL. Some of the services now available include:

- Network access to a HP 4000 laser printer and a Tektronix 450 color printer.

- Users have access to their home directories from any computer in the NSL. This is achieved in a user-transparent fashion through the cross mounting of file systems using NFS and Samba.

- Addition of an IMAP mail server. All of the NSL team uses a variety of systems on any given day. This mail server allows NSL personnel consistent access to e-mail from any computer inside and outside the INEEL firewall.

- Single, reliable network database of user, host, and network data. This was achieved using NIS+ and has greatly simplified the task of systems administration in the NSL.

Hardware and infrastructure improvements by themselves would not be optimally effective if a support system for users is lacking. This need has been addressed by the following:

- Online equipment scheduler—due to increased demand on NSL equipment, it became necessary to implement a reservation system. The NSL scheduler is available online at http://mira/vizlab/index.html. This system allows any employee of the INEEL to schedule NSL equipment for their use as well as providing a mechanism for resolving conflicts.

- Relocated all team members to the same area on the first floor of the EROB—previously NSL team members were scattered throughout the EROB. This was inconvenient for the team and troublesome for others who needed to find a NSL team member. Now it is easy for anybody using the NSL to find a team member when needing assistance.

- Origin 2000 programming class—to increase the knowledge and productivity of the NSL user base, the NSL sponsored a two-day class focusing on programming the SGI/Cray Origin 2000. Several other classes were held in the NSL during the past year.

- Reorganized web pages—a complete set of web pages to describe all aspects of the NSL.

It is easier than ever for users of NSL resources to access applications, data, printing, and e-mail. At the same time system administration has been streamlined, and system availability has increased.

To increase the comfort for users working in the NSL, several changes were made to the physical layout of the lab:

- Machine room enclosure—to improve cooling and to reduce noise, most of the large equipment has been separated from the rest of the lab by a floor to ceiling partition.

- Improved ergonomics—by adding better chairs at the workstations.

- Rewired lighting—lighting may now be controlled to provide different coverages, i.e., for the use of the projector, or use of the workstations, or one end lit and the other end of the room dark.

These changes not only made the lab more comfortable and convenient, they also improved the appearance of the lab. The lab is now a suitable place for giving demonstrations to groups of people. Since these changes have been made, at least 30 presentations have been given in the NSL using the projector and assorted equipment.

Numerical Optimization and Data Formats

INEEL users are running dozens of numerical simulation codes on the NSL hardware. Many of these are modeling extremely complex and tightly coupled phenomena involving diverse environmental concerns at the INEEL. In many cases these calculations take prohibitively long and hence limit the users ability to perform their analysis at the level of detail required by the problem. Therefore, a number of efficiency improvements are being pursued to enable more effective utilization of existing computational resources. These include scalar and parallel code optimization and a standard data storage format.

Scalar optimization is the process of reviewing single processor code and determining changes that decrease the runtime. The INEEL has many scientific applications that require large amounts of computing time to complete. Reducing the runtime of these applications on a single processor is the first step in code optimization. This provides an immediate benefit to the code users by reducing the time required to perform a particular simulation. It also allows for longer, more complex simulations to be run and for a greater number of users to gain access to these capabilities

An example of scientific code that could benefit from a decreased runtime is a 2-D finite element code written for KAPL. The code currently runs on *Orion*, the SGI Origin2000 machine located in the NSL. The WorkShop Debugger tool available for the SGI machines has several performance analyzer tools. These tools provide useful options such as determining bottlenecks, getting ideal times, tracing I/O activities, tracing page faults, finding memory leaks, and many more. Once the performance analyzer has located trouble spots in the code the analyst can attempt to correct them with the appropriate optimization techniques. The code was modified to try to improve its performance. Blocking or tiling could improve data locality at the multiple levels of the memory hierarchy. Overhead can be reduced by loop unrolling and in-lining small subroutines, which often increase program efficiency.

A systems engineer from SGI/Cray was brought to the INEEL to present a course about the SGI compiler options and code optimization. This course had approximately a dozen attendees and was well received. The course was helpful in explaining how the compiler can be used to optimize code, and how the performance tools can be used to decide which sections of the code to optimize. Several real world examples supplied by the attendees were used as examples for the class. This provided for a learning environment more closely attuned to the attendees and immediate benefit to the supporting programs through more efficient code.

Scalar optimization of code is an efficacious way for the scientists and engineers at the INEEL to be more productive. Many scientific codes such as the KAPL 2-D finite element code fail to obtain the desired speed even after scalar optimization. The next step after all of the scalar optimization has been completed is multi-processor optimization.

Multiple processor code optimization or parallel programming is the process of breaking up the tasks in a single code into optimally sized pieces, distributing the tasks between processors, and coordinating communication between tasks. When parallelizing the code, the number of processors available, the type of work to be performed, the location and size of available memory, and the amount of message passing necessary to coordinate tasks must be considered to find the optimal component size for each processor.

Another issue that must be considered is the computer's memory structure. The shared memory model and the distributed memory model are two of the most common approaches used for multiple processor memory. In a shared memory model all of the processors have memory reference access to all of the memory available. In a distributed memory model each processor has its own memory and can only indirectly access memory belonging to other processors. If code is written for a specific memory model it will not necessarily be portable to machines that do not use this memory model. One way to avoid the portability issue is to use one of the evolving parallel programming standards such as the Message-Passing Interface (MPI). MPI addresses the issue of portability, but may provide slower code due to its generic nature than code that was written specifically for the desired memory model. An existing MPI code was compiled and run on the Origin2000 to ensure that MPI was working correctly and to evaluate the overall effectiveness and efficiency of the hardware and software. The results were very satisfactory with linear, and occasionally super-linear, speedups being obtained.

The KAPL 2-D finite element code did not need to be ported to different machines; hence it was decided to use the shared memory parallel routines provided by SGI with the Origin2000. The first step in developing the parallel code was to optimize the scalar code. Once the scalar code had been optimized it was decided to use the automatic parallelization capabilities of the Power Fortran Accelerator (PFA) as an initial approach to the development of a parallel version of the code. The initial parallel code developed this way did not significantly increase the runtime. This was an unexpected result considering the complexity of such a large code. The -list option was used with PFA to produce a listing file that explains which loops were parallelized and why specific loops were not parallelized. The listing was analyzed and the code was rewritten so that more of the loops could be parallelized. Program directives were used to overwrite commands from the automatic parallelizer in cases where the changes that were made automatically were not the optimal change.

Reviewing listings generated by the automatic parallelizer revealed that many areas of code could not be parallelized due to data dependencies. The 2-D finite element problem is posed on a triangular mesh. One array is used to store the x and y values for each node and a second array is used to store the triangles and their node numbers. The present nodal number scheme prevented the automatic parallelizer to work optimally as it was unable to determine which memory locations would be referenced by a particular processor. This determination is necessary so that potential memory conflicts may be monitored and properly handled.

Domain decomposition would be required for the KAPL 2-D finite element code to be optimized on multiple processors. This is the primary mechanism used to exploit architecture-independent parallelism. An initial attempt at renumbering the nodes based on the number of processors was attempted. The new nodal numbering for each processor was viewed with the Advanced Visual Systems (AVS) to verify the mesh was correct. The parallel code was run with the new mesh ordering, but more work is required to find a better domain decomposition.

Parallel computing is an increasingly important core capability due to the ever lengthening runtimes caused by the greater complexity of today's scientific applications. Allowing these applications to run on multiple processors decreases their total runtime and increases users' productivity.

Another key to efficiently using computing and personnel resources is moving to a standard data storage and retrieval format. Such a format will allow for greater reuse of existing visualization and data analysis capabilities and remove one more burden from the application scientist. The ability to share scientific data without having to worry about platform dependencies is an important capability for the INEEL to develop and maintain. It is an added benefit that such a format is in wide use through the DOE Laboratory complex, the nation and the world. The Hierarchical Data Format (HDF) is a library- and platform-independent data format for storing and exchanging scientific data. HDF is developed and supported by National Center for Supercomputing Applications (NCSA) and is available free of charge from the Internet. HDF is the selected data storage format for the Accelerated Strategic Computing Initiative (ASCI) project, a combined effort between Los Alamos, Sandia, and Lawrence Livermore National Laboratories.

The NCSA HDF development team released a revision to the HDF4 libraries and an alpha version of the new HDF5 libraries. The HDF5 libraries address some of the limitations of HDF4, primarily by the addition of an object-oriented design and implementation while HDF4 follows a procedural model. HDF4 has a limit on the number of objects that can be stored and the file size. HDF5 does not have the objects or file size limitation and has a simpler more comprehensive data model. Hence HDF5 is much easier to extend but has had less time to mature than HDF4.

Selecting which library to use, HDF4 or HDF5, is not an easy nor a straightforward decision. HDF4 has passed the test of many years of use, but HDF5 has many new useful features. Significant differences exist between the two libraries, and at the present time no conversion between HDF4 and HDF5 is available. The initial decision was to use HDF5 as this was the new product and the most closely aligned with the DOE ASCI program. The KAPL 2-D finite element code output was converted to a HDF5 file. A HDF5 reader was written for AVS, and the KAPL data was displayed in AVS' graphics viewer. This was a successful endeavor and produced not only a workable data visualization and analysis tool but also much new insight into the behavior and applicability of HDF5. Related to these efforts, several members of the NSL team were invited as the first experts external to ASCI to review the data models and format work central to the ASCI code development teams.

HDF5 is currently an alpha release and not all of the options or capabilities are implemented in this release. The ability to query HDF groups had not been completed which made it impossible to make a generic reader that could be used for any HDF5 file. A Fortran interface is not available for HDF5 which is important since most INEEL applications are still written in Fortran. Due to these limitations and the experience gained with HDF5, the HDF4 libraries were used for the next code output task, the TETARD groundwater code.

TETRAD is a numerical reservoir simulator and is written in Fortran, so using HDF4 was the only choice available at the time. The HDF4 commands were added to the TETRAD code to produce HDF files following the same format as the original TETRAD files. Hence files could be used on any platform but still required the user to understand the TETRAD format and read them appropriately. A HDF file would be more useful if the user could read the files without having any prior knowledge about TETRAD's output format and this is one of the design requirements for HDF. Based on this philosophy, a more generic file format was produced and will be implemented for TETRAD by the end of the fiscal year. This will allow any analysis program capable of reading HDF4 files to read and manipulate the TETARD output files. Hence visualization and analysis functionality can be implemented in a single instance and yet be utilized across a variety of applications.

An AVS reader for HDF4 files that are output in the generic file format has been partially completed. The reader will allow users to quickly view their data output and manipulate it with a multitude of visualization algorithms. Since the applications are being modified to write data to the HDF files, the AVS reader will place the data in AVS. The user can than select the variables of interest and view the data in AVS' graphics viewer. AVS is the most commonly used visualization software system within the DOE complex and is one of the tools selected for the ASCI program. It runs on almost all computing hardware used at the INEEL and is maintained locally by the NSL team and worldwide by the vendor.

HDF is a very useful platform-independent data format that will allow scientists to easily share data internally and externally to the INEEL. Since HDF and several HDF tools are freely available from the NCSA, the HDF data can be easily viewed using the HDF tools. The AVS HDF reader will allow scientists to quickly view graphical displays of their data results. A problem with data results can frequently become obvious when the data is viewed in a graphical model. This is much more difficult when the data is viewed among large quantities of numeral output. The capability to develop platform-independent data formats that can be viewed quickly by the user continues to be a necessary core capability at the INEEL.

Three Dimensional Graphics

The NSL presently supports three areas of 3-D computer graphics—visualization, immersive environments, and visual simulation. Visualization is the process of representing abstract scientific data as images which helps in understanding the data. Immersive environments are computer generated sequences of images with which a user can interact by viewing, moving, rotating, and otherwise interacting with an apparently 3-D scene. Visual simulation is the process of imitating a real set phenomenon within an immersive environment by a set of mathematical formulas, which can simulate weather conditions, chemical reactions, atomic reactions, and biological processes. Visualization is most often used to gain greater insight into numerical data representing large, complex and tightly coupled physical processes. Immersive environments and visual simulation are used to convey some representation of reality for applications in training, accident preparedness, enhanced work planning and many other scenarios that can be safely and less expensively experienced within computer simulations.

Three toolkits and their corresponding application programming interfaces (APIs) are presently used for computer graphics—World Toolkit, Visualization Toolkit, and SGI Performer. World Toolkit is used primarily for immersive environments and visual simulation. Visualization Toolkit and Performer can be used for all three types of applications. Each has its own particular set of advantages and disadvantages and complements the others well for the diverse applications worked within the NSL.

An important aspect to immersive environments and visual simulation is realism. Realism is the ability to make a virtual world appear as correct as possible. This is extremely important for some applications. The effectiveness of training, accident preparedness, and some enhanced work planning applications is often directly related to the degree of realism. One method of obtaining realism is using textures and lighting. Textures in 3-D graphics are the digital representation of the surface of an object, such as a picture of marble or grass. Lighting is calculated from mathematical equations that govern how various types of light sources illuminate specific materials. Through the use of textures, a wall appears to be made out of marble, brick, or wood or some other material to help the user make a more substantial connection to the scene. We can also use texture to show how a terrain would look in a particular real world scenario, often with a photograph or videotape providing the needed imagery. Hence a great degree of realism may be obtained at a lower hardware and software cost, with the texture information taking the place of complex three dimensional objects. World Toolkit, Visualization Toolkit and Performer all provide support for both textures, and lighting. Performer has the best support for textures, providing ways to add moving and transparent textures, and many different lighting methods.

Physical objects (buildings, etc.), terrain, and some forms of numerical data represented by geographical metaphors can be shown as if viewed from any direction. This allows these computer representations to be interactively manipulated in the same fashion as one might wish for their real world counterparts. The different APIs all support a variety of input mechanisms, each of which can be used to control the observer's viewpoint. The NSL presently supports three physical types of input devices—traditional mouse, dialbox, spaceball and tracking. The two degrees of freedom of the mouse input is mapped to the surface of a sphere allowing the user to either translate or rotate in two dimensions. The dialbox and spaceball are both six-degree-of-freedom input devices allowing users to simultaneously and independently control each of the six variables x, y, z translation along with roll, pitch and yaw. Finally an electromagnetic motion tracking device is used to obtain position and rotation information for devices such as head mounted displays and data gloves. This information is input to the computer system at 120 Hz and is used to ensure that the location and orientation of the user's viewpoints and relevant avatars are correctly positioned.

Another important characteristic for immersive environments and visual simulations is obtaining consistently achievable frame rates. This is necessary if the user requires realistic motion cues such as the correlation of inner ear feedback to visual motion cues. When this is not adequately addressed, not only does the realism suffer, but users can become disoriented and even nauseous. Performer has the fastest rendering engine of the three APIs as it is produced by the same vendor as the hardware, allowing real-time creation of complex virtual worlds and visual simulations. The Performer product also contains the best performance analysis tools which can be used to identify bottlenecks and investigate potential solutions. It is, however, presently limited to hardware systems manufactured by SGI, which does not include everything within the NSL. The Visualization Toolkit is the next fastest, although its performance varies given the detail of the model. It has the distinct advantage of being freely available through public domain distribution and runs on almost every imaginable platform. Currently no official support structure exists although an extremely active worldwide user community has proven very responsive. A new company has been formed by the principal authors and will soon be offering a selection of support contracts. World Toolkit is a commercially supported product, as is Performer, but is comparatively slower. It also lacks the performance analysis tools of Performer but does contain many high level interfaces and is available on a variety of platforms.

An important aspect of many environmental management applications is related to terrain visualization. A specific geographic area at least sets the framework against which the various remediation and management practices will be set. In other cases, specifics of the terrain, such as elevation, aspect and gradient, can be critical factors that must be thoroughly and accurately represented and incorporated into the model. Often it is desired to incorporate satellite and/or high altitude photographic data to more accurately and completely model a given location. These data sets are often very large and complex and can significantly reduce frame rates or visual fidelity if not appropriately handled. Several different representational schemes along with level-of-detail models and large memories are used to provide a satisfactory result. Confounding this process even more are the multitude of file formats used to represent these types of geospatial data. Of the three APIs, World Toolkit supports none of the commonly used formats, Performer reads two and the Visualization Toolkit has been extended by NSK staff to read the Digital Terrain Elevation Model (DTED) format.

Due to the engineering emphasis at the INEEL, a number of software packages are used locally for creating 3-D models. Examples are IDEAS, ProEngineer, SolidWorks, and AutoCAD. Each modeling program stores the data in a different file format. It is very difficult to transfer models between the various modelers or the NSL software. This is a longstanding problem and many partial solutions have been used over the years. These have all been application-specific, expensive to maintain, and usually of little use when the next application arose. Capability now exists to use many of these formats through Performer, which supports over 30 file formats and is easily extendable to add new formats as needs arise.

Visualization Toolkit supports 12 formats while World Toolkit only supports two. Hence Performer has become the application of choice for this task and has continued to prove very useful when model translation is required. This has been a great efficiency enhancement since all models require translation at least once in the process of moving from the designer's desktop to the high performance visualization systems in the NSL.

Technical Society Participation

In addition to their roles within the INEEL, NSL team members continue to maintain a DOE, national, and international presence in the visualization and high performance computing community. NSL team members have organized and chaired conferences and technical sessions, reviewed technical contributions, presented both reviewed and invited papers and tutorials, and maintained a general presence in these international communities. The DOE Computer Graphics Forum, ACM SIGGRAPH, IEEE Visualization and the annual INEEL Supercomputing Conference are examples of conferences in which the NSL team members have played significant roles. These team members also hold elected positions in numerous user groups including the Cray User Group, Sun High Performance and Data Center Group and the AVS User Group. In these and other capacities, INEEL personnel have gained increased recognition and are frequently asked to respond to queries from around the country and the world.

Milestones

The EMS task had four milestones designed to monitor progress throughout the year. All milestones were met on time or ahead of schedule. These milestones help guide the efforts during the year to produce an effective, integrated computing environment for the challenging environmental problems faced by INEEL scientists and engineers. The first of these milestones was the submittal of a purchase request for upgrading the existing computing environment within the NSL. The system was selected based on compatibility with existing INEEL and DOE computing structure, well defined product future, hardware and software performance characteristics. Additionally its architecture is optimally suited for the types of environmental problems presented by current and future INEEL work scope.

The other three milestones centered on the design and implementation of advance visualization capabilities within INEEL programs. This included the creation of a Small Group Display Environment where teams could interact with interactive high-resolution displays in an effective manner rather than trying to crowd around a monitor or share copies of output. Existing INEEL groundwater simulation code supporting the remedial investigation and baseline risk assessment was coupled to the advanced visualization capabilities of the NSL. This new capability is now available to the scientists at their desktops and in small group settings. This provides an efficient and effective end-to-end tool for the analysis and communication of simulations modeling the movement of contaminants through the subsurface under and around the INEEL.

Summary

Large strides have been made in improving the capabilities of the NSL. The improvements that have been made in hardware, infrastructure, and systems integration at the NSL have been a good first step. The NSL team has met their goal and demonstrated that a viable high performance computing and visualization environment can be built to meet the needs of INEEL scientists and engineers. The NSL offers INEEL users an efficient and effective computing environment at a higher level of excellence than previously available.

A number of tools for code analysis and optimization have been installed and are in use within the NSL. These are benefiting all INEEL users by providing quicker runtimes, more rapid turnaround of results, facilitating longer and more detailed simulations, and allowing access to a greater number of users thanks to more efficient use of available resources. The number of users familiar with the new tools has grown substantially, and they are becoming new sources of expertise within the INEEL. The adoption of a standard data format has reduced the burden on the application scientists, increased the number and quality of visualization tools available, and aligned the INEEL work with ASCI, the nation's premier scientific computing program.

In the past year, the capabilities of the NSL have increased to the point where visualization, immersive environments, and visual simulation are now ready for application to a multitude of environmental applications. All of these areas, separate or combined, have importance in environmental management. Through visualization coupled with immersive environments one can actually see impacts of certain decisions on the environment before a project is implemented or a building is erected. Visual simulation helps predict mistakes and prevent them through event and training simulation resulting in enhanced work planning. Together these activities have provided a foundation of computational capabilities that are required by INEEL scientists and engineers to efficiently and effectively perform their present activities and provide a well planned growth path for the future.

COMPUTATIONAL SCIENCE

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Scope And Objectives

The Office of Environmental Management (EM) soon will be making expensive and long-lasting choices from among a wide range of new technologies, processes, or strategies for remediation, alternative manufacturing processes and products, and stewardship of legacy wastes, among others, as part of its obligation to manage environmental issues. The computational science project is intended to give EM the ability to make informed choices among the variety of proposals for the disposition of waste. Our ultimate goal is the trustworthy, even if only qualitative, prediction of the outcome of a wide variety of proposed technologies, processes, or strategies that might be employed in environmental management. Secondarily, we might also be able to propose improved solutions for environmental problems. Specific FY-98 tasks were as follows:

1. BEOWULF
2. Chemical and transport processes in complex interfacial systems
3. Complex dynamics of fluids and solids
4. Fracture propagation in solid components
5. Determinism in time series

Technical Accomplishments

Background

The relationship between Computational Science tasks and environmental concerns can be illustrated by considering the problem of storing a solution of hazardous waste in a faulty container. Figure 1 illustrates how Computational Science can relate to this particular environmental concern.

Of course, these objectives require in principle calculations and predictions for all kinds of systems, microscopic, and macroscopic. Here we focus on the chemical or transport behavior of materials under conditions that might be encountered in systems employed to solve EM problems. As the example in Figure 1 illustrates, chemical and transport processes for materials are prominent in many EM problems. Even with this focus, the scope is enormous. Therefore we confined our scope to five topics. These are, on the one hand, rich in application to EM problems at the INEEL and at other DOE sites, and, on the other hand, are sufficiently compact for investigation within the resources of the CCTE program.

This year (February–September 1998), we concentrated on building or upgrading modeling capabilities that will be required by anticipated applications. Therefore we planned to either purchase advanced modeling software, when unavailable commercially, or to write it ourselves. Next we planned to test it and then integrate it into existing software. Following are the specific objectives for each of these tasks [task leader,* other staff (if any)]:

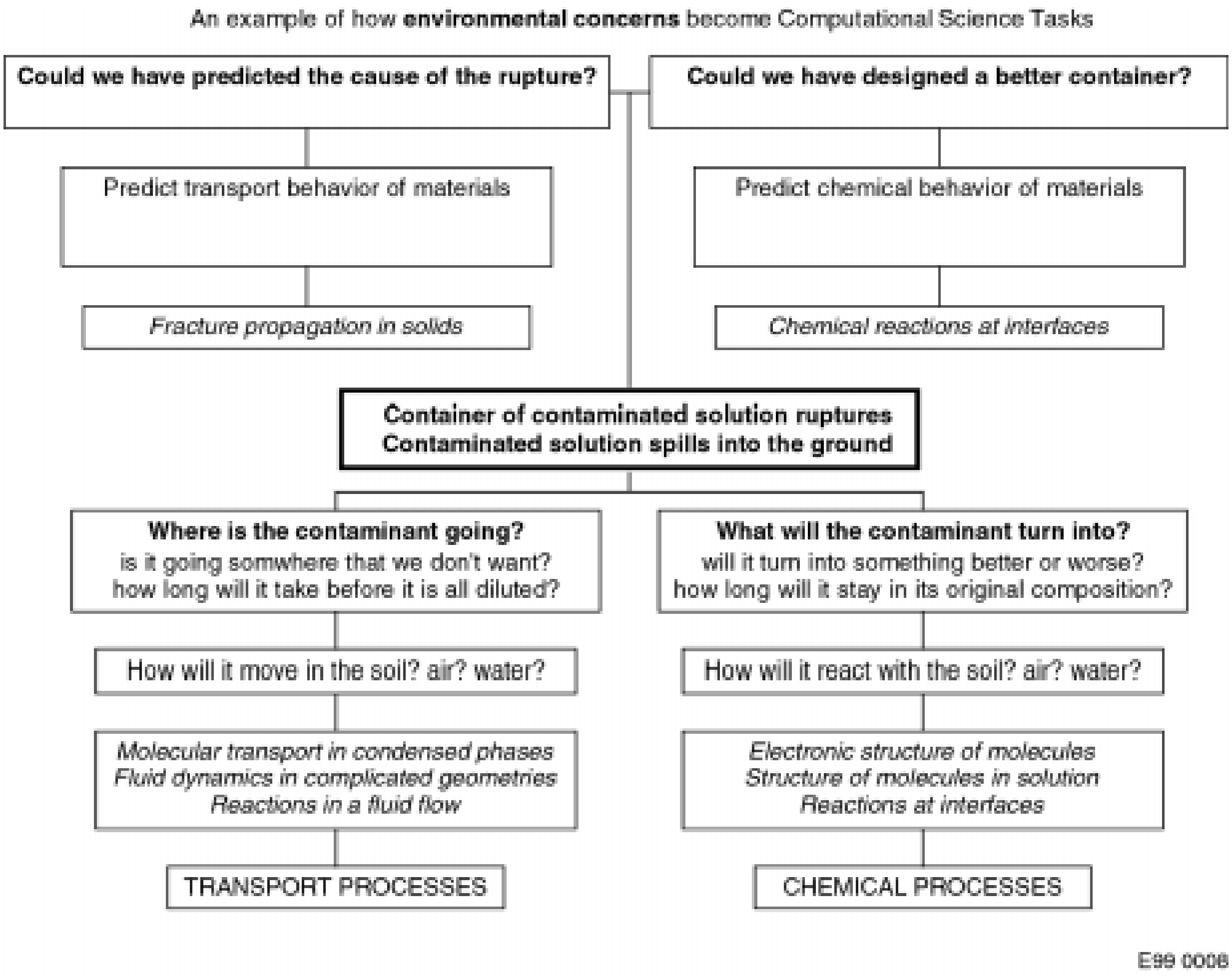

Figure 1. How environmental concerns become Computational Science tasks.

Objectives for BEOWULF

The recently acquired Origin 2000 (O2K) from Silicon Graphics Inc. (SGI) is the centerpiece of newly acquired computational capabilities. With 24 R10K processors and 6 GB of shared RAM, the O2K is the logical replacement for the CRAY supercomputer, whose acquisition over a decade ago launched serious computational work at the INEEL (see Environmental Modeling and Simulation Project). As a general-purpose machine that readily compiles both modern and legacy code, the O2K is in constant demand, providing the capacity required by a large body of diverse users. Although the O2K also could perform very well as a high capability machine, its high expense forces us to employ it primarily as a high capacity machine. In order to provide high performance computational capability, albeit to a limited number of users with specialized codes, we have decided to acquire the components for a BEOWULF parallel processor. The BEOWULF design consists of commodity cpus and network (FastEthernet) switching systems in order to achieve maximum capability for minimum expense. Its low cost allows us to consider dedicating it to a few users, even though it cannot serve a large user body, because it can only compile specialized code. Experience with a similar installation at LANL this summer suggest that we may expect an order of magnitude in speed over that typically experienced with the O2K, for a price of an order of magnitude less than the O2K. The O2K will continue to support this Project's tasks that use commercial or general-purpose code. BEOWULF will provide high performance for all of this Project's tasks when specialized code is supplied. Some of the Project tasks for FY-99 in this Project call for acquisition or development of the specialized codes required for this system.

Objectives of Chemical and Transport Processes in Complex Interfacial Systems

Our primary objective this year was to build the computational tools required by applications that employ molecular simulations and modeling of chemicals, materials, and their processes. Our second objective is to identify or clarify important problems to be addressed by molecular simulation and modeling in following years. Molecular simulation is especially called for in circumstances where the controlling entity of a process is either too small or too short-lived to be easily accessible to experiment. Furthermore, the ability to explore contemplated processes realistically, at a molecular level, permits a level of prediction well beyond that of simple theories. Therefore molecular simulations can become an important part of a designer's toolkit when exploring chemical or materials processes for solutions to EM problems.

Objectives of Complex Dynamics of Fluids and Solids

This task is aimed at development of modeling tools that will enable more realistic simulations of the complex dynamics of deformable continuous and discontinuous systems with increased understanding of their underlying mechanics (and geophysics), chemistry, biology, and thermodynamics.

By way of background, we observe that most bodies, astronomical, geological, biological, engineered, or otherwise are mixtures, in which two or more constituents co-exist. If one of the constituents is preponderant and the other constituents essentially insignificant, the body is usually assumed to be of the predominant single constituent. However, there are innumerable situations where none of the constituents present in the body can be ignored with respect to the others; e.g., plasmas or high temperature gaseous mixtures, biological tissue or muscles, slurries or suspensions, porous rocks or soil infused with water or oil, and growth of microvoids oxidizing metal with strength degradation. Sometimes, the constituents in a mixture undergo chemical reactions, usually resulting in an interconversion between the constituents and the formation of new compounds. Sometimes the constituents of the mixture are even different phases of matter, moving at different velocities, having different temperature ands stress states, and dynamically exchanging mass, momentum, and energy between the phases. This latter type of mixture flow, with interpenetrating motion of dissimilar materials, is known as multiphase flow. Because this interpenetration has features useful in modern technology (e.g., the promotion of mixing in chemical reactors), as well as features that are destructive (e.g., the erosion of pipe walls in pneumatic conveying equipment), the theories of mixtures and structured multiphase flows have been developed over the past several years to provide a rational framework for studying these types of problems. The solution of flows with large deformation of multiple materials remains a major area of research and development. However, even though disagreement exists on the proper set of conservation and balance equations for multiphase mixtures, with several interesting issues remaining unresolved, sufficient progress has been made and various theories have been applied successfully to model some of today's most difficult flow problems. Because of the complexity of these models, solutions are only tractable through numerical approximation and simulation of these highly dynamical physical processes. The availability and even applicability of numerical solution methods for many of today's complex flow problems is clearly lacking.

In the past, a significant number of INEEL tasks have involved a need for mixture modeling. Often, however, adequate modeling capability was unavailable, not just at the INEEL, but anywhere. It is evident that even more tasks in the future will benefit from improved modeling methods for dynamic multiphase mixtures. To support this growing need, this effort was divided into two tasks designed (1) to investigate a novel class of Lagrangian methods, broadly termed "particle" methods, for applicability to complex fluid and solid dynamics, and (2) to acquire as broad of range multiphase flow simulation capability (commercial or otherwise) as possible, or begin development of such capability for use at INEEL.

Objectives of Fracture Propagation in Solid Components

Oftentimes the usefulness, lifetime, or safety of material systems or components is determined by defects or fractures. The ability to simulate and predict the behavior of such fractures is thus very important. Because of the large stress and strain gradients and microscopic spatial scales involved, fracture modeling is one of the more challenging aspects of solid mechanics computations.

In the past, a significant number of INEEL tasks have included the need for fracture modeling. Consequently, the necessary capability and expertise to simulate static or nonpropagating fractures has been well established. Such simulations are clearly limited, however, since fractures naturally propagate. This task involved the development of computational capability and expertise to simulate propagating fractures in both elastic and elastic-plastic materials. The task has clear ties to a number of existing and planned projects at the INEEL. It also directly supports other core capability efforts, specifically those within the materials dynamics area.

Objectives of Determinism in Time Series

This task is devoted to developing and publishing a robust computational technique for the detection of determinism in possibly noisy time series. Many experiments, from the laboratory to field studies, can be expressed as the measurement of a time series. We expect to advance the state-of-the-art in the detection of determinism (e.g., periodicity) in complicated time series by exploiting recent advances in Time-Based Clustering (TBC) and fuzzy logic. Applications, although deferred here, are expected to apply to a vast range of experiments and field studies (e.g., barometric fluctuations in the subsurface). This task was undertaken to continue to extend the current theory of symbol train analysis through advancing the TBC algorithm recently invented at Utah State University. Symbol train analysis is the basis for detection and modeling of complex systems such as chaos. TBC is a new concept that lends itself to modeling complex signals that are comprised of varying basic time constants within their phase plane. This project was centered on publishing the initial concepts of TBC within the Chaos community, and exploring how best to port the existing TBC tools from the Macintosh to UNIX and Windows operating systems so that they might be more widely used and tested.

FY 1998 Accomplishments

BEOWULF. The BEOWULF system was scheduled to be installed by the end of January. However, because of the imposition (or re-imposition) of the OMB-mandated Year 2000 moratorium on new computer equipment, the purchase of the BEOWULF components was delayed until early September. The components are being ordered at the time of writing this report.

Chemical and Transport Processes in Complex Interfacial Systems. The most important accomplishment for this task was the evaluation, purchase, installation, and validation of a proprietary suite of chemical and materials simulation software. This suite, purchased from Molecular Simulations Inc. (MSI), and consisting of over 20 software modules so far, provides an interactive environment for molecular modeling with the following capabilities:

1. Semiempirical and first-principles electronic structure calculations of atoms, molecules, clusters, surfaces, and solids. These calculations provide, among others, the energy, band structure, electronic density-of-states, optical (uv/vis/ir) spectra, phonon modes analysis, and transition-state structures.

2. Structure and dynamics calculations of condensed phases and interfaces with empirical force fields. These calculations provide, among others, the energy, temperature, pressure, free energy, time correlation functions, transport coefficients, and chemical reaction pathways.

3. Prediction of products from chemical reactants.

4. Properties of polymers derived from group contributions and conformations.

5. Analysis of x-ray crystallography data.

6. Three-dimensional animated color display of simulations and analyses.

7. A software developer’s toolkit for incorporating nonproprietary source code.

The evaluation culminated in a live demonstration at the INEEL by MSI early in March. The first order of software was approved for order, purchased, received, and installed on the SGI Origin 2000 at the INEEL by May. Additional modules were ordered and received in July. An initial onsite training session was conducted by MSI in June, followed by training for the PI and Mr. Propp at MSI headquarters in September. Testing with sample problems began as soon as the software was installed.

After the results of sample test problems were compared and shown to agree with the known solution, a more difficult problem, with an unknown solution, was considered, i.e., mercury transport in chalcopyrite. Chalcopyrite, along with other layered sulfur compounds, is under consideration at the INEEL for reversible mercury storage. A molecular-dynamics simulation was set up in only a few hours with the MSI software that incorporated mercury atoms in a crystalline chalcopyrite host. Preliminary results indicated that mercury transport in chalcopyrite is infrequent with single mercury atoms, but may occur rapidly for clusters of mercury atoms that first swell the chalcopyrite lattice. This picture is in agreement with subsequent x-ray data (analyzed with other modules of the MSI suite), and with the general trends observed by the real-time electron microscopy of more strongly layered sulfide compounds. A thorough investigation of the mechanism of mercury transport and uptake in layered sulfide compounds has been identified as a subtask in the work planned for FY-99 in support of other experimental CCTE work (see Chemical Separations Task). Our purpose here was simply to exercise the package on a difficult (and unsolved) problem to understand its behavior. We found that the package had no difficulty either in quickly setting up the problem, or in carrying out the simulations. Finally, the PI took training for the Software Developer’s Kit (SDK) by MSI, a module that allows non-MSI applications to be attached to their Visualizer GUI. The SDK will prevent the obsolescence of earlier code written at the INEEL, and will expand the usefulness of the MSI suite as codes from other sources are acquired.

As part of the identification of environmentally significant problems to be supported by this Project, the PI provided assistance to the Chemical Separations Project through a collaboration with Prof. John McCoy (New Mexico Tech) and his student Joanne Budzien, both supported by the Chemical Separations Project. A theory of gas solvation in polyphosphazene polymer membranes was worked out along the lines of Flory-Huggins, Hildebrand, and Bicerano, which involves the contribution of chemical groups in the polymer to gas solvation. Essential to this work was the identification of the group contribution due to the phosphorus in the phosphazene backbone, which was carried out primarily by Ms. Budzien. Her work provides the first empirical basis for the phosphorus group contribution, which heretofore had been guessed poorly in the literature. Ms. Budzien plans to join this Project for FY-99 after finishing her M.S. in Materials Engineering for more advanced work on chemical separation membranes before continuing her Ph.D. work. Prof. McCoy will continue to provide guidance to the Chemical Separations Project in FY-99. Other accomplishments for this objective included the establishment of a collaboration with Dr. Lawrence Pratt of LANL and the PI for the development of a theory of solvation in aqueous solutions. Discussions held at the March Meeting of the APS and at the INEEL led to tasks in chemical and transport processes in complex interfacial systems for FY-99. A paper resulting from discussions begun in January was published in Molecular Physics, which lays the foundation for an alternative approach to the study of the structure and thermodynamics of aqueous solutions. A collaboration with Dr. Robert McGraw of BNL, the PI, and Dr. Berry was established for pursuing nucleation studies, particularly, nucleation in a flow. These have become tasks in both chemical and transport processes in complex interfacial systems and complex dynamics of fluids and solids in FY-99. Finally, a postdoctoral fellow for FY-99 has been identified (Andy Vaught from Arizona State) to work on the development of electronic structure code for condensed phases on BEOWULF.

Complex Dynamics of Fluids and Solids. Traditional modeling of deformable continuous (and discontinuous) media employs grid-based numerical methods. Although grid-based modeling methods can be very powerful, they are unsuited to handle some complex “fluid” behavior such as formation of droplets, mixing of streams, turbulent flow, and gas/liquid interactions. They are also unsuited to handle chemical or biological reactions at the molecular or atomic level. Recently, there has been a disjointed growth of interest in numerical methods that do not require grids, or which require grids for only part of their operation; here we refer specifically to what we are calling “particle methods.” Particle methods (of which there is a variety) represent grid-free Lagrangian methods that are appealing as alternatives to the numerical techniques currently used to analyze complex, highly dynamical material motions. However, it appears that, for various reasons, none of these methods have the full range of capabilities needed for modeling complex processes. Because of the limited development and application of these methods on the one hand, and because on the other hand they have shown significant, or even unique, merit for the solution of certain complex dynamical events, this research task was initiated to characterize and clarify the advantages and drawbacks of various particle methods. This task was initiated to extend current research on these approaches to develop new capabilities of interest to the INEEL and DOE.

A systematic literature review revealed that the particle methods could be divided into two broad categories: (1) those that approximated the conservation equations directly by approximating governing partial differential equations, and (2) those which attempted to simulate a physical phenomena directly without representing it with partial differential equations first. The first, and largest, category includes smoothed particle hydrodynamics (SPH), particle-in-cell (PIC), fluid-implicit-particle (FLIP), material point method (MPM), and reproducing kernel particle method (RKPM). Closely, related to these methods are those that are not truly particle methods but in a similar philosophy attempt to solve governing field partial differential equations on grid-free or arbitrary mesh point (arbitrary connectivity) domains. These methods include multi-directional finite difference scheme (MDFD), weighted least squares method (WLSM), interpolating matrix method (IMM), element-free Galerkin method (EFG), diffuse element method (DEM), and the moving least squares method (MLSM). The second, and smaller, category includes the quasi-particle method (QPM), particle-and-force (PAF), and the NABOR method.

After review of all these methods this task was narrowed, based on our current assessment of present and future need, a smaller and more manageable subset. Initially, we have focused our efforts to include acquisition of FLIP methodology through the CFDLIB codes, to be discussed in the next section, and further investigation of SPH, QPM, PAF, and NABOR like methods. We brought Prof. Donald Greenspan (University of Texas at Arlington) to the INEEL to give a seminar on QPM. It became apparent that while QPM was capable of qualitatively representing a diversity of interesting complex flow phenomena, its quantitative tie to physical bases was lacking. However, when aspects of the PAF and NABOR-like methods are coupled with it, a richly tractable method may result. We will continue pursuing this line next fiscal year. We began writing SPH, QPM, and PAF codes to simulate basic phenomena for comparison purposes. This effort will also continue.

Originally, we had anticipated acquiring a commercial reactive, multiphase flow code in addition to the research codes already available. However, after reviewing the functionality of the commercially available codes, their licensing structures, their costs, and ease of researcher (user) modification, we decided that none fit our research needs sufficiently well to justify its acquisition. We instead decided it would be better, at least initially, to team with another DOE laboratory (LANL) on an ongoing code they have been developing for the past few years. This code, CFDLIB, is really a library of computer codes capable of solving a wide variety of computational fluid dynamics (CFD) problems in two and three dimensions. CFDLIB offered most of the basic capability we desired as well as the research flexibility we needed without the hindrances of commercial software, i.e., we have source code and can modify it at will to solve specialized physics for specialized problems. The cell-centered finite volume codes are related by a common multiblock data structure for efficient processing on supercomputers and an arbitrary Lagrangian-Eulerian (ALE) split computational cycle. Volumes in the library cover all flow speed regimes from fully incompressible to hypersonic and enable multifluid and multiphase computations with an arbitrary number of fluid fields, each with their own set of conservation equations. The design of each code volume in the library is modular, making development of codes for specialized applications quicker.

Unlike commercial software, the CFDLIB code volumes are developed with the sophisticated computational physicist in mind. The experienced computationalist can set up and solve a large variety of problems, but, necessarily, with little instruction from code manuals and internal documentation. CFDLIB, it is emphasized, is a research tool, most useful to us in exploring highly specialized effects in complex flow problems. Consequently, significant effort is required on our part to implement, maintain, modify, develop, and participate in this effort. The codes create realistic simulations by pulling together the physical models used to represent the effects of chemical species conversion, physical kinetics of phase change, granular flow, multiphase turbulence, and other complex interactive flow processes. The equations that embody these physical models are developed using a combination of detailed mathematics, definitive laboratory experiments, and physical intuition. The simulations then bring together these diverse sets of information in order to test the validity of theories and to provide important guidance to the design and operation of modern equipment and processes. We are using CFDLIB as a vehicle for the exploration of problems in complex material dynamics and are adapting it to create specialized analysis tools. For example, we have begun the creation of a simulation tool to model the Top-Down Spray Coating Process (Porous Material Development) for the processing of thin adsorbing/absorbing coatings on particulate/bead media in a fluidized bed spray dryer (please refer to the Top-Down Spray Coating Process section of this report for more details). Some CFDLIB modules are serving in the basis of this code.

The FLIP scheme (a sophisticated descendent of the PIC method) has also been incorporated within the CFDLIB structure. Consistent with the particle methods section above, FLIP is a particle-based method with extremely low numerical dissipation which offers distinct advantages for highly deforming material flows, and in chemically reacting and multiphase flows. FLIP has been diversely applied to model magnetohydrodynamic flow in the earth’s magnetosphere and the sun’s heliosphere, to model plasma processing tools, and to model solid mechanics. The solid mechanics version of FLIP uses the “material point” method and has been applied to the study of high explosives. In this application the material point method eliminates the need for mixture theory by evaluating equation of state and strength models particle by particle. Thus, the properties of the plastic binder, explosive granules, and gases that are evolved by the decomposition of the explosive, are each modeled accurately; their interaction is captured by the solution of dynamical equations on a grid in the usual way. This application is not unlike other mixture applications of interest to the INEEL (e.g., methane hydrate decomposition). For this task, Dr. Berry visited Dr. Bryan Kashiwa of LANL and discussed some problems and strategies for CFDLIB. Since the codes are under active development, new versions are released a couple times per year. We obtained CFDLIB97.2 and implemented it on two engineering workstations in sequential execution mode, the SGI Origin2000 and a H-P J200. The codes were updated with subsequent changes. The GNU "make files" (open software foundation modular code build commands) were rewritten to run on the PC using both Lahey and Digital Visual Fortran packages. Several test problems were run and compared with known solutions, either analytical or from other software. We began testing a new chemical kinetics module to be eventually incorporated into CFDLIB. Later, we also implemented the latest release CFDLIB98.1 on the SGI Origin2000 in sequential execution mode. While this version is functionally the same as CFDLIB97.2, the structure and modular build instructions were totally revised to utilize the C-preprocessor. A test problem was run with this new version and appears correct. CFDLIB98.1 also has the new parallel execution constructs for which we were waiting before attempting parallel implementation on the SGI Origin2000; this will probably be delayed to the next fiscal year. As mentioned above, at the end of this task, a model was begun of the Top-Down Spray Coating Process. So far the particle entraining gas flow and the counter impinging atomization gas flows have been included in a geometrically realistic 2-D fluidized bed vessel model with a porous baffle plate included to distribute the suspending gas flow and hold the particles when no gas is flowing. This work is anticipated to continue. As an appendage to this task Dr. Berry met with Dr. Robert McGraw, BNL, to discuss some collaborative work with coupled in-flight nucleation and growth (condensation) of interesting constituents from an expanding and/or cooling flow stream. This work will extend our previous work to incorporate a stronger direct coupling between the gases and particulate in each volume rather than indirectly along streamlines as was previously implemented. This research will benefit both plasma quench reactor processing of waste or hazardous materials and formation of desirable products from supercritical fluid expansion (at INEEL) as well as aerosol formation and transport in the atmosphere (at BNL).

After extensive initial investigation, several particle methods were carefully selected and further development was begun. Further assessment will depend upon our further development and testing on realistic, but complex, problems at hand such as break-through and plate-out flows in porous media, degradation of solid materials, highly deformable flows where history dependence of moving properties is critical, etc.

The evolving CFDLIB family of reactive, multimaterial and multiphase codes was implemented in several forms on our computer systems. The development of this software is necessarily an ongoing theoretical and programming effort in which we must remain involved with the LANL team. We have already begun development of simulations to support the Porous Materials Development task utilizing this software as a foundation. This problem and others are sufficiently complex that single processor implementation gives extremely slow turn around. Therefore, parallel implementation will be pursued shortly. Based on our FY-98 effort, we are in a position to continue our efforts with increased focus on building viable simulation tools in these two categories. Based on our teaming with BNL, we are also in a good position to improve upon our ability to simulate novel in-flight nucleation and growth of important constituents from expanding, cooling flow steams, to benefit ongoing INEEL and BNL environmental process developments.

Fracture Propagation in Solid Components. The task began with a review of existing fracture propagation computational techniques. Although many key references were already collected, a more systematic literature review was warranted as a first step in the effort. Next, a relatively simple fracture propagation capability was developed, based on finite element mesh debonding as dictated by a computed fracture criterion. Then a more mechanistic approach was investigated, wherein microscale void growth was included to identify the initiation of a crack front. Where possible, the approaches were assessed by comparison to existing applicable experimental data.

An exciting result of the literature review is a powerful new fracture propagation modeling technique called the Arbitrary Local Mesh Refinement (ALMR)[1] method. It is being developed at the

University of California Davis. Since this technique showed clear promise for improving INEEL core capabilities, the proposed work scope (described above) was enlarged to include investigating this new method. This effort resulted in a beneficial collaborative arrangement with U.C. Davis and significant improvements in INEEL computational capability, as will be described below.

Simple Mesh Debonding Methods

One of the simplest methods used to model propagating fractures in continua utilizes standard computational meshing (e.g., finite elements) but permits systematic disconnection of the mesh in regions where crack growth is expected. Predefinition of the fracture path enables the technique to adequately adjust the remaining connected model to take into account the effects of the crack growth process. Using this basic method, different fracture processes can be modeled revealing the evolution of stress, strain, and displacement during crack growth. Fracture of materials with properties ranging from brittle to very ductile can be simulated using variations of this simple mesh debonding technique. In fracture mechanics, the behavior of a material is typically characterized using a variety of experimental specimens; two of the more common are the compact tension (CT) and the three-point bend bar. Utilizing the commercial finite element analysis program ABAQUS,[2] mesh debonding numerical experiments were developed for each of these specimens.

For the CT geometry, brittle material properties were assumed and crack movement governed by the level of a critical stress component a specified distance ahead of the crack tip. Once the critical value is attained, the material is locally debonded. Ductile material properties were used with the three-point bend specimen, with mesh release governed by experimentally measured crack length and load line displacement as a function of time. With both specimens, the mesh debonding technique provided qualitatively reasonable results, describing the crack propagation history and the evolution of the stress, strain, and displacement fields. Recent three-point bend fracture experiments using A710 steel were used for direct comparison to the numerical results. Figure 2 shows the resulting plastic deformation at the onset of crack growth. In this model, the crack path has to be predefined and the actual crack path did not remain perfectly straight.

A third, more complex, numerical experiment was also conducted. In a current INEEL program (DOE-BES, Mechanically Reliable Surface Oxides) the behavior of cracks in brittle oxide coatings during thermal excursions is being investigated. As a demonstration, an oxide formed across the sharp corner of a metal substrate was modeled using multiple predefined potential crack paths. The technique was effective in showing the energy transfer from bulk material to incremental crack advance. In the simulation, a single crack would extend, releasing energy and redistributing the remaining energy to other areas of the component. In areas where additional potential crack paths had been defined, the surplus energy was often sufficient to extend these cracks. Computed stress contours from a typical calculation are provided in Figure 3, showing stress concentrations at crack tips in the oxide. Note that although five potential crack paths were defined, conditions were only favorable for crack growth along four, and each of the four propagated a different length. For the case involving a single crack, the final crack length and stress field predicted with the debonding technique compared very favorably with a series of static crack simulations, providing quantitative verification of the approach.

In general, it was demonstrated that simple mesh debonding techniques are easily implemented and appear to work well for the geometries investigated. The technique is thus very useful for geometries that are intentionally designed to result in specific crack trajectories. However, it has been observed in actual crack growth experiments that even with simple geometries, the crack path can deviate due to very small geometric or materiel property irregularities. As a result, the debonding method has the significant limitation that the crack path must be known *a priori*.

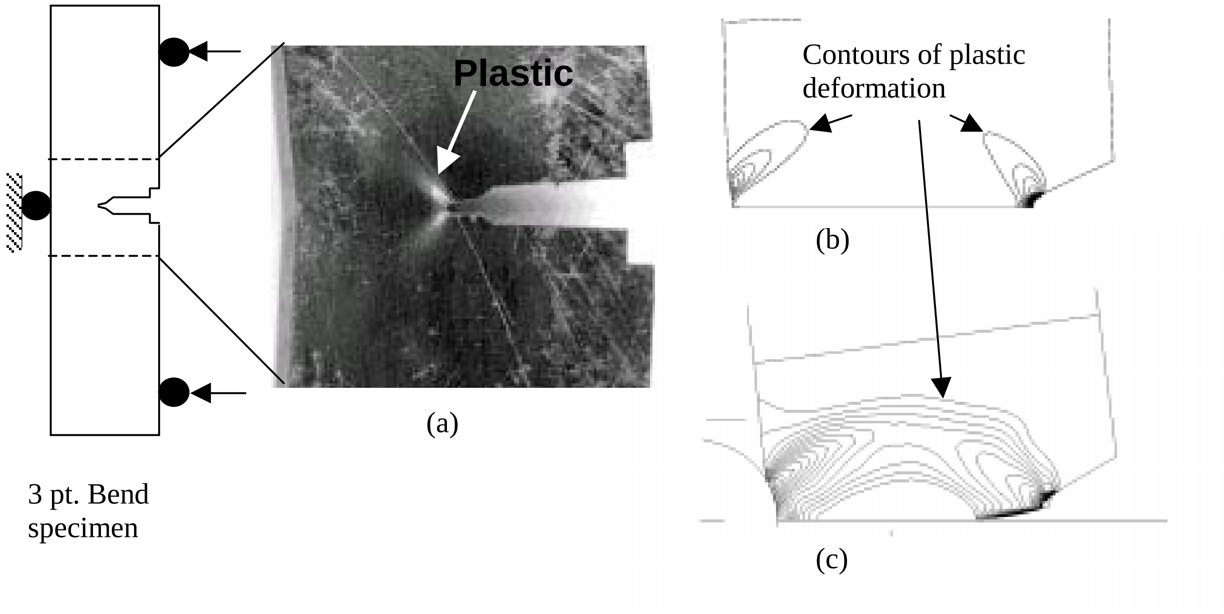

Figure 2. Plastic zone development at initiation for three point bend specimen(a) and model(b). Fully developed crack growth and plastic strain predicted by model(c). [Exploiting symmetry, half of the specimen was modeled].

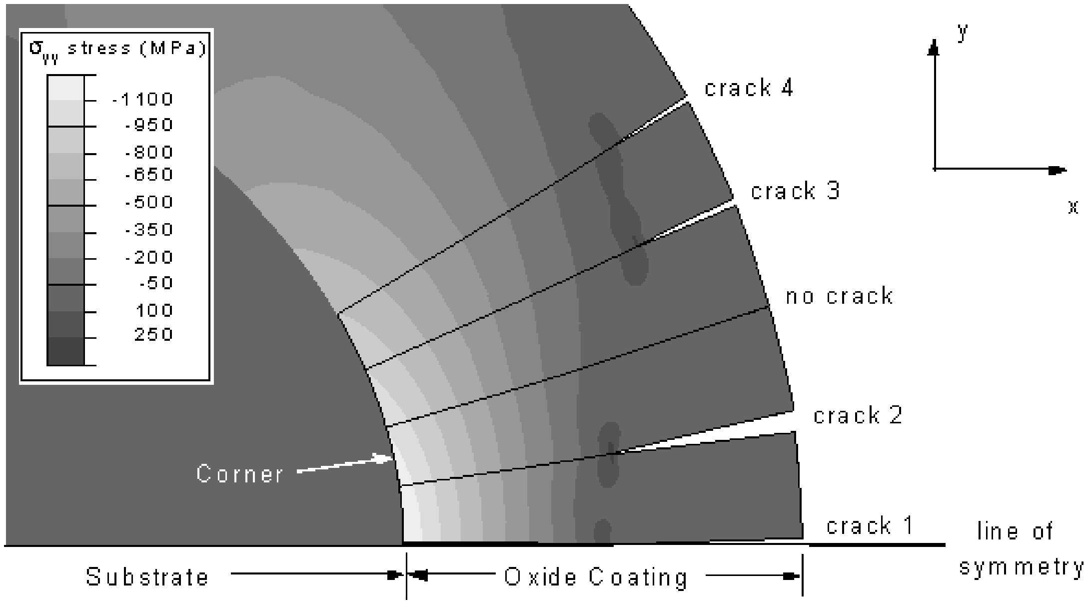

Figure 3. Multiple crack growth model of brittle coatings.

Void Growth Methods

The formation, growth, and coalescence of micro defects such as voids is the main mechanism for damage and fracture of engineering materials.[3] In an effort to accurately account for these mechanisms, a refinement of general plasticity relations to include the effects of void growth was incorporated. The Gurson[4] constitutive relation allows for a model to take into account the changing capacity of the material to carry load and plastically deform as a void grows within an element. This model was developed in 1977 by Gurson[4] in an attempt to adequately describe the observed material response of engineering materials. Tvergaard[5] later refined the constitutive relation and a version of this formulation is what was used to investigate how this model responds to imposed boundary loads. The Gurson[4] constitutive model was used to compare the numerical results of an axisymetric bar loaded in tension. The Gurson material description resulted in “shear band” plastic deformation at high load states that were not observed in the plasticity solutions. This is in response to the material formulation to lose load carrying capacity as the void grows. Less material is available as the strain hardening material responds and as a result, the model developed shear bands. Other implementations of the Gurson method are in material systems having a set of Gurson-type void cells in the crack path with the rest of the material being modeled using general plasticity. While these research algorithms seem to hold promise in accurately modeling the void growth and coalescence systems, the necessity of predefining the crack path is a significant limitation.

Arbitrary Local Mesh Replacement (ALMR) Method

Currently all commercial finite element programs that model crack growth, require user definition of the complete crack path. Although this is satisfactory for carefully designed experimental specimens with controlled geometries, in the real world the critical crack path is strongly governed by the changing geometry, material behavior and loading. The ALMR method,[1] mentioned above, eliminates the restrictive requirement of knowing the crack path a priori. Upon learning of this new technique, the investigators contacted the original developer, Dr. Mark Rashid of the University of California, and invited him to the INEEL for further discussion. Dr. Rashid provided a seminar on the ALMR method that was well attended and very well received. A collaborative agreement was reached that evolved into a summer appointment for a graduate student and transferal of the research software to the INEEL at no cost. Specifically, during a six-week appointment, the graduate student, Tonya Emerson, was able to load, compile/run the software, update the user manual, and provide a demonstration to the computational group.

An interesting example of the ALMR capability is provided in Figure 4, showing the predicted crack advance in a rectangular plate containing a hole. This problem can be considered a rather severe test of the ALMR method: the crack path is curved, and unknown in advance; and the patch mesh intersects an interior boundary of the domain during the course of the solution.[1] The effect of the hole’s presence is plainly evident in the crack path, as well as in the variation of the critical stress with crack arclength.[1] The crack path curves in response to the altered direction of maximum principal stress directly beneath the hole.[1] The algorithm is capable of modeling the advance of a crack front while taking into account the influence of the flaw as the crack tip advances. Clearly this new technique provides an INEEL capability well beyond that previously available.

The collaborative relationship with U.C. Davis, if continued, will allow for the continued infusion of leading edge modeling capabilities to the INEEL at little or no cost. As future efforts come into focus, we envision supplying U.C. Davis with experimental results to validate the numerical models. This will involve the continued connection via students to optimize the synergistic relationship. Both U.C. Davis and the INEEL will benefit from continuing this collaboration.

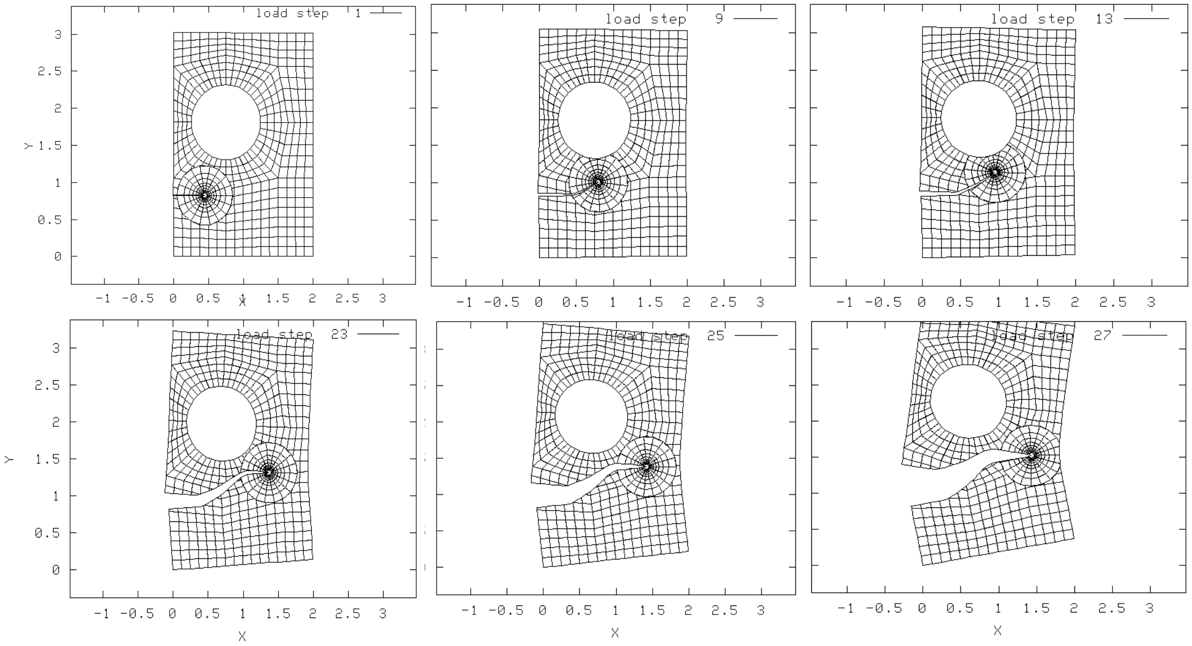

Figure 4. Progress of an advancing crack as simulated using the ALMR finite element method.

In addition to the linear elastic ALMR method, Dr. Rashid is finishing work on an elastic-plastic version of the code, which he has also offered for our use at no cost. As a natural extension of this work, Dr. Rashid would like to develop a 3-D formulation. The planned INEEL work scope for FY-99 includes on-campus support for Ms. Emerson, to facilitate the 3-D code development.

In conclusion, the simulation of crack growth using simple mesh debonding was demonstrated for a variety of geometries, materials, and loading conditions. The methods are easily implemented using commercially available finite element software, and appear to work well for the cases considered. Results were qualitatively reasonable and, where comparisons with experimental data or other simulations could be made, quantitatively accurate. The major limitation of the mesh debonding technique is that the crack path must be known before the simulation can be performed. Preliminary efforts were made to enhance the simple mesh debonding technique for ductile materials by employing localized constitutive models permitting void growth and coalescence. Specifically, the Gurson constitutive relationship was used to compare the deformation development and the impact that such effects might have on crack initiation, growth and coalescence. The ability to include void growth effects to predict where crack initiation is likely has been demonstrated with subsequent crack extension using a predefined crack path. Most significantly, a collaborative effort was established between the INEEL and Dr. Mark Rashid at U.C. Davis. As a result, a powerful state-of-the-art crack propagation algorithm (ALMR) has been implemented, tested, documented, and demonstrated at the INEEL. Continued collaboration will result in further enhancements to the software (e.g., plasticity and 3-D capability) and verification via experimental data.

Determinism in Time Series

The initial goal of publication of the Time-Based Clustering (TBC) concept has been met through a peer reviewed conference paper in the ANNIE ’98 conference. This paper will also be included within an ASME book published from the conference. Another paper has been written and is currently being submitted to NASA Tech Briefs for publication.

A second goal for this project was to study and port the TBC tools developed by the Dr. Tolle as a member of the Rocky Mountain NASA Space Grant Consortium. This portion of the project was initially planned around the use of a Metrowerks Latitude Library developed for porting MacOS code to Unix-based environments. However, due to Apple Computer's change in development goals, the Latitude library by Metrowerks was discontinued. Therefore, a new effort was made to study other alternatives for porting the toolbox. This effort has focused on the use of Tcl/TK, a scripting language and a GUI C-based library. Tcl/TK has current implementations on a majority of current state of the art operating systems. These include the most important operating systems to our operations: Windows, Unix, and MacOS. The initial study has almost been completed. The Tcl/TK solution appears to be an acceptable, if not a more improved, method for easy porting and further development of the TBC tools. Tcl/TK appears to allow concurrent development of the TBC tools for all three major operating systems with no or minimal code changes.

Summary of the Computational Science Project

We fulfilled our objective of building (or rebuilding) our chemical, transport, or materials modeling capabilities by acquiring the needed tools in the following ways: direct purchase of advanced molecular modeling software from a vendor, acquisition of advanced fracture propagation software via university collaboration, acquisition of advanced fluid dynamics software via national laboratory collaboration, and writing of advanced time-series software here at the INEEL. We have just begin carrying out our goal of installing a BEOWULF parallel processing machine for high performance computations. We have in the meantime successfully employed the general-purpose machine acquired under another CCTE project.

Here we conclude with a summary of some accomplishments February–September 1998:

Peer-reviewed publications (*authors from the INEEL):

1. L. R. Pratt and R. A. LaViolette,* "Quasi-Chemical Theories of Associated Liquids," Molecular Physics 94, 909–915 (1998).
2. J. L. Budzien, J. D. McCoy, J. G. Curro, R. A. LaViolette,* and E. S. Peterson,* "The Solubility of Gases in Polyethylene: Integral Equation Study of Standard Molecular Models," Macromolecules (in press, 1998)
3. C. R. Tolle* and R. W. Gundersen, "Searching for Determinism in Erratic Signals Using Fuzzy Clustering of Delay Vectors," accepted for ANNIE '98 (Artificial Neural Networks In Engineering), Nov. 1–4, 1998, St. Louis, MO (in press, 1999).
4. C. R. Tolle* and L. Allred, "Time-Based Clustering Symbol Train Creation," NASA Tech Briefs, (submitted, 1998).

Conferences attended (attendee):

1. March Meeting of the American Physical Society, 16–20 March, Los Angeles CA (LaViolette)
2. First NWChem Workshop, 23–25 March, Pacific Northwest National Laboratory, Richland WA (LaViolette)
3. American Institute of Aeronautics and Astronautics Joint Conference, 13–16 June, Albuquerque, NM (Berry)

4. 13th U.S. National Congress of Applied Mechanics, June 22–26, Gainesville, FL (Steffler)

5. North American Materials Science User Group Meeting, Georgia Institute of Technology, 21–23 July, Atlanta GA (LaViolette)

6. 128th Meeting of the American Chemical Society, 26–31 August, Boston MA (LaViolette)

7. Second NWChem Workshop, 1–3 September, Pacific Northwest National Laboratory, Richland WA (Propp)

INEEL presentations sponsored (sponsor):

1. Prof. Donald Greenspan, Department of Mathematics, University of Texas at Arlington, "Particle Modeling for Fluid Dynamics," 5 May (Berry)

2. Prof. Mark Rashid, Department of Mechanical Engineering, University of California at Davis, "Finite Element-Based Simulation of Fracture in Arbitrary Two-Dimensional Domains," 13 May (Steffler)

3. Dr. Keith Glassford, Molecular Simulations Inc., "Introduction to Materials Modeling," 20 May (LaViolette)

4. Dr. Lawrence Pratt, Los Alamos National Laboratory, "Molecular Modeling of Hydration: Temperature, Pressure, and Chemical Effects on Aqueous Solutions of Hydrocarbon Gases," 28 July (LaViolette)

5. Mr. David Wright, Center for Solid State Science, Arizona State University, "Electron Microscopy of Intercalation in Layered Transition Metal Dichalocogenides," 20 August (LaViolette)

6. Mr. Andy Vaught, Department of Physics, Arizona State University, "Direct Density Functional Energy Minimization on a Finite Element Grid," 15 September (LaViolette)

Collaborations established (INEEL contact):

1. Prof. Mark Rashid and Ms. Tonya Emerson, Department of Mechanical Engineering, University of California at Davis (Steffler)

2. Dr. Lawrence Pratt, Los Alamos National Laboratory (LaViolette)

3. Dr. Bryan Kashiwa, Los Alamos National Laboratory (Berry)

4. Dr. Robert McGraw, Brookhaven National Laboratory (Berry and LaViolette)

5. Prof. John McCoy and Ms. Joanne Budzien, Department of Materials Engineering, New Mexico Institute of Mining and Technology (LaViolette)

References

1. M. M. Rashid, "The Arbitrary Local Mesh Replacement Method: An Alternative to Remeshing for Crack Propagation Analysis," *Computational Methods, Applied Mechanical Engineering*, 1998, 133–150.

2. Computer code ABAQIS (Hibbitt, Karlsson, and Sorensen, Inc., Providence, RI, 1997).

3. S. Yi, C. Eripret, and G. Rousselier, "Influence of Defect Shape on Damage Evolution and Fracture Behavior of Ductile Materials," *Engineering Fracture Mechanics*, Vol. 51, No. 3, pp. 337–347, 1995.

4. A. L. Gurson, (1977), "Continuum Theory of Ductile Rupture by Void Nucleations and Growth: Part I—Yield Criteria and Flow Rules for Porous Ductile Media," *Journal of Engineering Materials Technology* 99, 2–15.

5. V. Tvergaard, "Influence of Voids on Shear Band Instabilities under Plane Strain Conditions," *International Journal of Fracture Mechanics*, Vol. 17, pp. 389–407, 1981.

COLLECTION AND INTEGRATION OF NON-EM DOE SCIENCE

J. A. Seydel

Scope and Objectives

This program identified software needs for four areas of environmental research at the INEEL and found sources, within and without the DOE Laboratories, for that software. The areas are

- Calculation of steam condensation front propagation during steam-enhanced extraction to remove volatile or semivolatile organic contaminants in fractured porous media
- Computer simulation for imaging situations that arise in characterization of spent fuel containers or operator/radiographer training for radioactive waste characterization
- Environmental modeling on Beowulf-type commodity supercomputers.
- Development of the conceptual framework for integrating components being developed by other DOE labs, federal agencies, and the scientific community into a decision support system for future management of DOE lands. Completing the full scope of this effort will take two to three years.

Technical Accomplishments

Implementation of the M2NOTS Code at the INEEL

Principal Investigator: Glenn E. McCreery

Background. M2NOTS (Multiphase Multicomponent Nonisothermal Organic Transport Simulator) is considered the premier code for modeling steam-enhanced extraction (SEE) of contaminants from porous media. M2NOTS is an extension of the TOUGH2 code[1] that can simulate one, two, or three dimensions, model isothermal and nonisothermal environments, model multiphase and multicomponent flow with phase change, and model porous and fractured media. It is a fully compositional simulator, that is, the nonaqueous phase liquid (NAPL) may consist of any number of user-specified chemicals and each chemical is allowed to partition into all phases. It can model mass and heat transfer in the vesicular basalt flows that underlay the INEEL during SEE or other waste remediation processes such as vapor vacuum extraction and electrical heating of soils for contaminant removal. It can also be used to study NAPL migration in contaminated soil. M2NOTS has been used to model the thermohydrological response of high-level nuclear waste in unsaturated fractured porous media (modeling of Yucca Mountain by Sandia).

Professor Kent Udell of the University of California at Berkeley and his students have experience with M2NOTS. They assisted in code acquisition, documentation, and verification. Professor Udell also presented a seminar at INEEL entitled "Steam Enhanced Extraction of Non-Aqueous-Phase-Liquids from Soils and Groundwater."

FY-98 Technical Accomplishments. The code was tested by analyzing steam-enhanced extraction experiments that were conducted at the INEEL in FY-97.[2] SEE consists of steam injection into porous media, which may be unsaturated with water or partially or completely saturated with contaminated water. The contaminants are swept along with the steam condensate towards an extraction well where water and vapor are removed. The experimental apparatus contains a porous media test section, which is a locally full-scale representation (on the small end of the size range) of a fractured basalt matrix. The basalt matrix is simulated using 90 rectangular glass blocks (5.1 cm x 7.6 cm x 3.8 cm) with thermal properties similar to basalt. Fractures are simulated by gaps between the blocks. The simulated fractures are both horizontal and vertical. The fracture fill material is simulated with 1.0 mm glass spheres. The test section is mounted in a stainless-steel framework with Teflon insulation laminated inside the inlet and outlet plena. Triple-pane, argon-filled windows provide visual and photographic access. A steam generator provides constant steam mass flow rate as a function of immersion heater power.

The experimental apparatus was modeled initially using the grid shown in Figure 1. The matrix blocks and fractures were subsequently subdivided into a finer grid with 600 nodes, the maximum permitted with the present version of the code. Calculations were performed for several experiments in which the matrix was either initially water saturated or unsaturated. Experimentally determined condensation front positions for one experiment with initially water saturated conditions are shown in Figure 2. Calculated temperature profiles for the same experiment are shown in Figure 3. The calculations provide reasonable predictions of the condensation front data, although the temperature profile is flatter than the data due to the coarse nodalization. Other calculated quantities, such as steam saturation profile, are also reasonable, but indicate that finer nodalization is needed.

SEE may be useful for trichloroethylene (TCE) removal near an injection well at INEEL. Modeling of the vadose zone, which consists of layers of vesicular basalt, with M2NOTS would be part of an investigation of TCE cleanup via SEE.

Summary. The objectives of the project—(1) implementing the M2NOTS code at the INEEL, and (2) testing the code by comparing calculations with data for steam injection in fractured porous media experiments—were accomplished successfully. The comparisons indicate that the code needs to be modified to permit an increased number of nodes, especially if vesicular basalt that underlies the INEEL is to be modeled in the future. Other accomplishments of the project include:

1. Professor Kent Udell of the University of California at Berkeley presented a seminar and provided consultation to a number of INEEL personnel.

2. Interest was generated in the possibility of using the Steam Enhanced Extraction process for removing TCE contaminants at the TAN injection well. Professor Udell agreed to provide Robert Starr of the INEEL a "white paper" outlining the suitability of the method for the site and an estimate of energy, cost, and time requirements. A more extensive investigation of TCE cleanup using SEE would involve M2NOTS modeling of the TAN vadose zone.

3. Glenn McCreery, Kent Udell, and his graduate students agreed to pursue writing a conference paper on the comparisons of code calculations with experiments.

Nondestructive Examination (NDE) Simulation

Principal Investigator: Timothy A. White

The INEEL has extensive capability in x-ray imaging, including real-time radiography, digital radiography, and two- and three-dimensional computed tomography (CT). These imaging systems vary in x-ray energy used, time and spatial resolution of the detector system, and configurability, including size and material constituents of the object to be imaged and portability of the system. Because of the wide variety of imaging scenarios, it is often impractical to quickly “mock-up” an imaging system when asked “Would it be possible to see *this feature* in *that container*?” A more efficient method would be to quickly and accurately simulate the imaging situation. A variety of x-ray imaging scenarios in the environmental arena could be addressed with a simulation capability. For example, in characterization of spent fuel

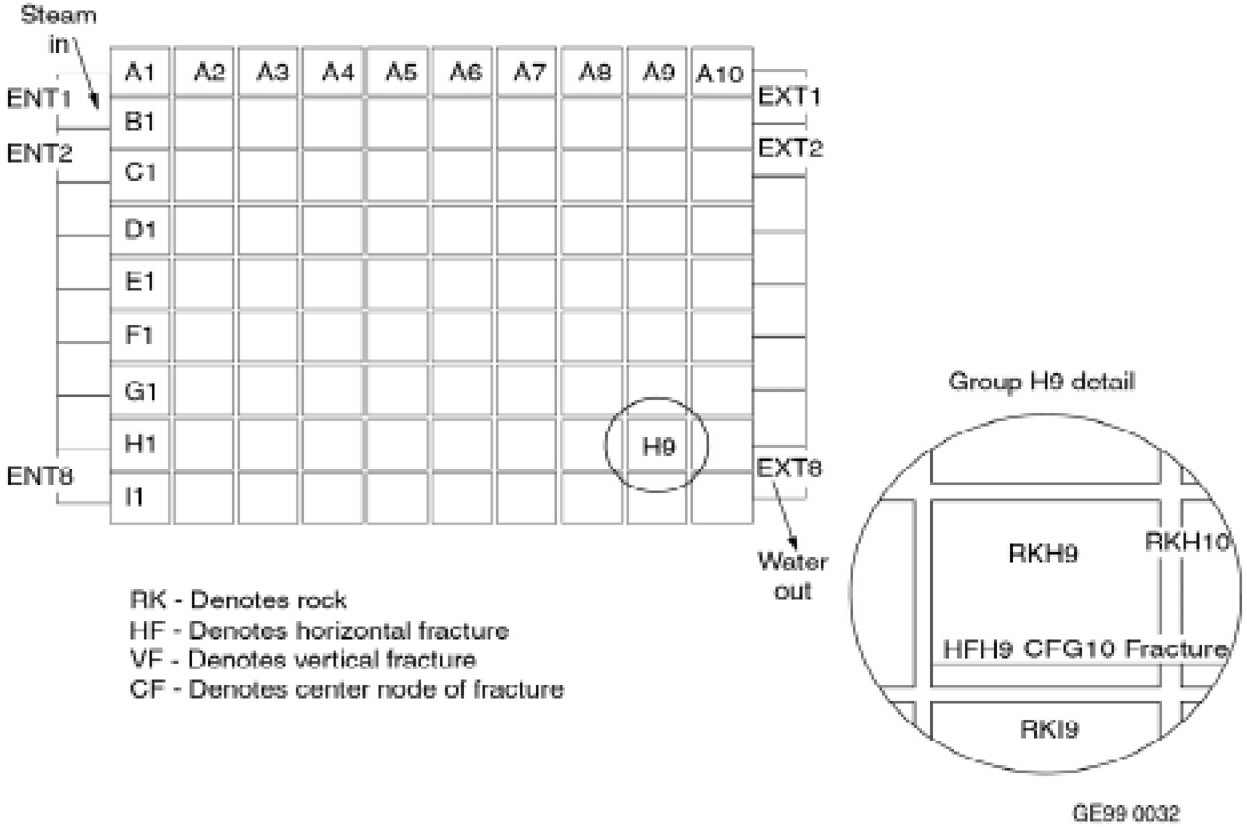

Figure 1. M2NOTS grid distribution and nomenclature.

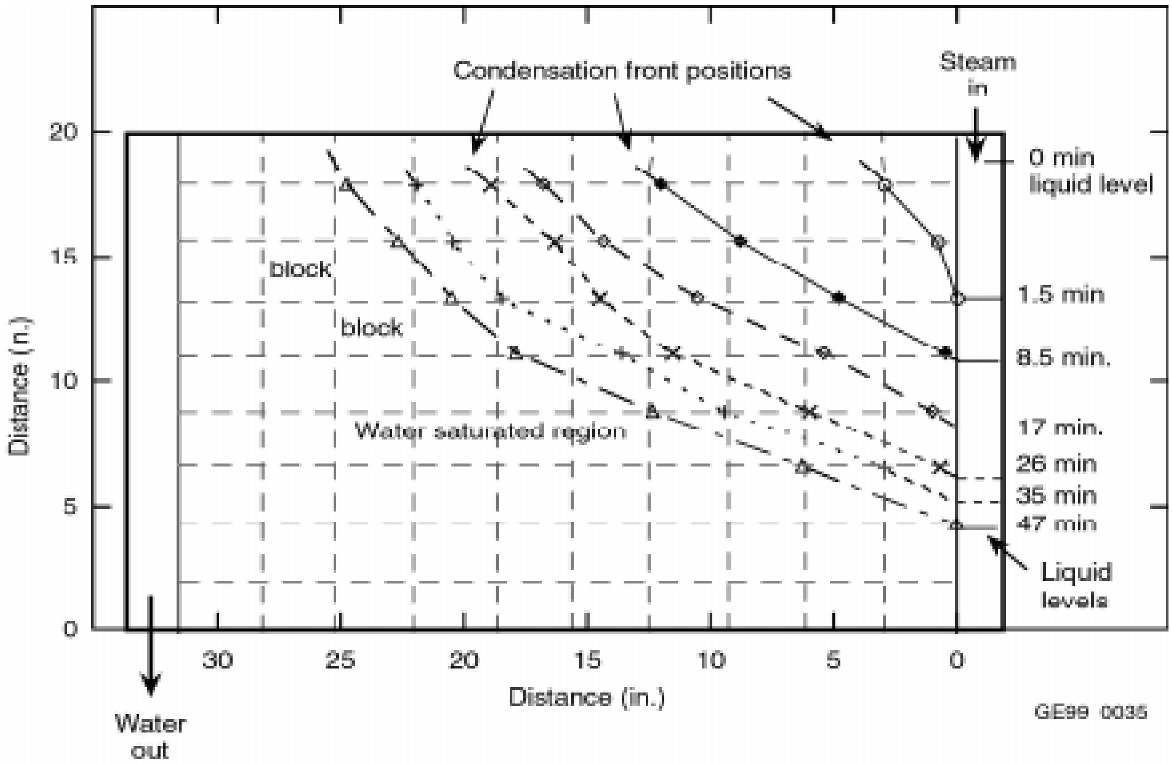

Figure 2. Position of the condensation front: experimental data for steam injection rate of 15 g/min. Injected steam saturation was 100% (no liquid content).

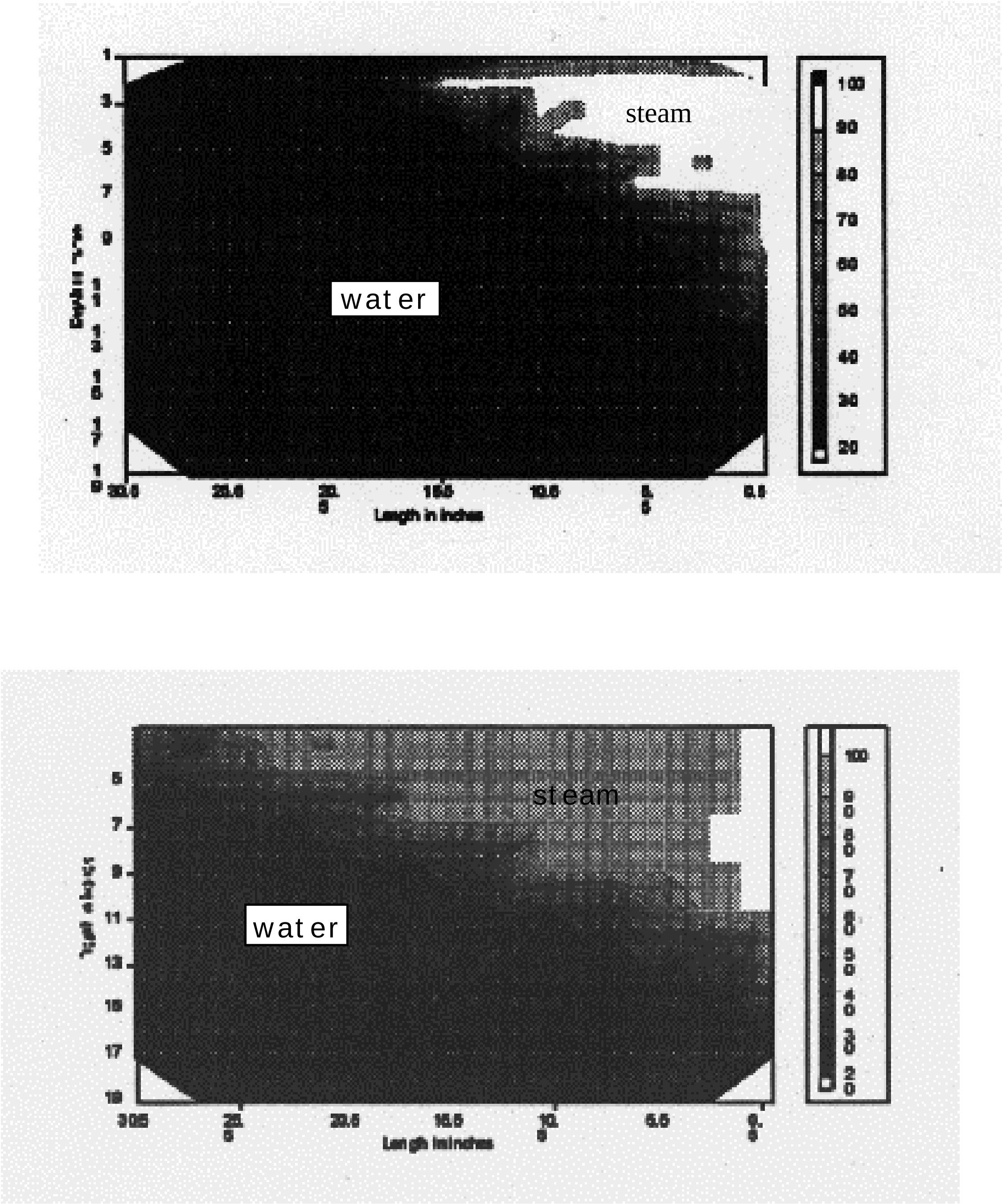

Figure 3. Calculated fracture temperature profile at 4.2 and 20 min (250 and 1200 s). (Block temperatures not shown.)

containers the position and integrity of fuel bundles, container integrity, and presence of voids or liquids need to be determined. This raises questions such as can a transmission radiograph (which gives insight about the internal contents) of a spent-fuel container be obtained in the presence of the gamma-ray emission background of the container itself? Or, in an environment in which there is limited access to the object, can a few images taken from different perspectives give enough information about the position and integrity of the material in the container? Without a simulation capability, preliminary questions such as these have to be answered by building a prototype system and testing it in a potentially harsh environment.

Simulation capability would also be useful for operator/radiographer training. Training operators for interrogation of waste drums as a certification step before shipping to the Waste Isolation Pilot Plant facility requires an x-ray facility unless adequate training can be achieved through simulation. A simple to use, accurate, and reasonably fast program that can simulate drum imaging could be very useful.

FY-98 Technical Accomplishments. This task surveyed the simulation capabilities that are available (predominantly at national laboratories and universities), determined which packages meet our criteria, brought those packages to the INEEL, tested them on relevant simulated objects, and evaluated them for our applications.

Three criteria were used to evaluate the simulation packages, ease of use, accuracy, and speed.

- Ease of use: it must be simple to manipulate the imaging geometry and straightforward to display and evaluate the resulting image

- Accuracy: the simulation must accurately model the physics of x-ray imaging, including the effects of Compton scatter, beam hardening, and detector resolution

- Speed: simulations must take only a reasonable amount of time.

There are obvious trade-offs between these criteria—it may not be possible to perform an accurate simulation, especially of a complicated part, in a reasonable amount of time. Partly for that reason, the criteria are ambiguous; for instance, a “reasonable amount of time” may be a function of the accuracy of the simulation.

There are two general categories of simulation code. Ray-tracing algorithms calculate the path length through the object along a line of sight between source and detector and then calculate the attenuation of x-rays due to material along that path. In general, algorithms based on the ray-tracing approach offer fast calculations at the expense of inaccurate models of imaging physics. Monte Carlo algorithms track individual photons as they pass from the source to detector, incorporating interactions between the photons and material in the object by randomly sampling the probability distributions that govern the underlying physics. Algorithms based on Monte Carlo calculations tend to be very slow, but are often the standard by which the accuracy of simulated data is judged.

Four packages were chosen for evaluation at INEEL, three ray-tracing packages and one Monte Carlo simulation package:

- XRSIM from the Center for Nondestructive Evaluation, Iowa State University. This is an X-windows (Unix-based) ray-tracing package that includes simulation of a variety of bremsstrahlung sources and takes a CAD model as the object to be imaged. Features: simple to use and fast.

- HADES from Lawrence Livermore National Laboratory. This is a Unix-based ray-tracing package that uses CAD input files and poly-energetic sources. Features: easy to use, fast, simulates data for CT. (This program has not yet arrived from LLNL.)

- The MIRL package, from the Medical Image Research Laboratory at the University of Utah. This is a ray-tracing package that uses combinations of simple shapes (right circular cylinders, ellipsoids, elliptical Gaussians) as objects, and simulates only single-energy x-ray sources. Features: complicated to use, point detectors, fast simulations of CT data, useful for investigation of CT misalignments.

- MCNP from Los Alamos National Laboratory. This is a Monte Carlo simulation package that has been developed over the past 30 years (it is the granddaddy of simulation codes). Features: extremely complicated to use, computationally slow, very configurable (can simulate anything), very accurate results.

It is apparent that a single program will not meet all of the above criteria. Although some of the ray-tracing algorithms incorporate beam hardening (XRSIM, HADES), no algorithm of this type adequately simulates the physics of Compton scatter. For x-ray imaging with an area detector, scatter is a major detriment to image quality—scattered photons tend to reduce the contrast and spatial resolution of an image, inhibiting the ability to image small, low-density features such as voids. Thus, if the purpose of a simulation is to determine if it is possible to see a small void region in a high-density object such as a spent nuclear fuel container, the ray-tracing code will produce incorrect, falsely encouraging results. And, although the Monte Carlo code does an excellent job of simulating the imaging physics, the program is too slow and much too cumbersome to be used as a routine simulation platform.

However, it is also apparent that both types of programs have utility. XRSIM, for instance, is very straightforward to use—within a few hours of obtaining the code, it was possible to simulate the radiograph of a munition. The simulation looked remarkably similar to an actual radiograph as is shown in Figure 4. In cases where low-density objects are being imaged (where scatter is not a concern), for quick testing of an imaging setup, or for training of operators, the window-based ray tracing algorithms are more than adequate. In fact, the group responsible for developing a system to train INEEL radiographers to characterize waste drums has expressed an interest in XRSIM as a possible training tool.

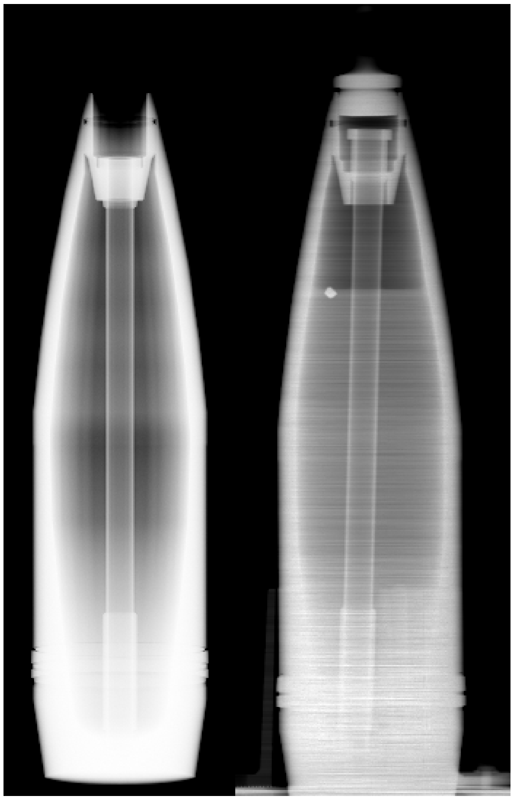

Figure 4. Radiograph simulated with XRSIM (left) and radiograph collected with linear-detector array (right).

A definite use for the Monte Carlo code also exists, even though it is slow and difficult to use. Any time a quantitative image is desired, in situations in which scatter is important, for example, MCNP is the best of the simulation options we have acquired. Or in the case of imaging an object that is emitting gamma rays—none of the ray-tracing options are capable of simulating "hot" objects. However, the ramp-up time to use MCNP is long; at this point we are only able to simulate very simple objects. It is also not clear whether MCNP is the best Monte Carlo option for imaging; MCNP was designed to track any type of particle, and is best suited for single-detector simulations. The capability to perform Monte Carlo simulations is essential to our ability to simulate (predict the results from) complicated imaging tasks; MCNP may not be the optimal solution, but it is a program that we can utilize.

Simulated images from XRSIM and MCNP are compared to actual radiographs collected in the Digital Radiography and Computed Tomography Laboratory in the figures below. In Figure 4, a simulated radiograph of a munition obtained with XRSIM and a radiograph of a 155-mm munition obtained with a linear-array detector are shown. This simulation took a few minutes to set up (although it took considerably longer to draw the part) and less than a minute to calculate. Although this is not a clean comparison—the real data is a fanbeam projection and the simulated data conebeam—the simulated data looks remarkably like the real data.

Notice, however, that near the bottom of the munition (where the walls are nearly 25 mm thick), the simulation shows more detail than the actual radiograph. This difference is probably due to the inadequate simulation of scatter—even though the real data has very little scatter (since it is from a linear detector array), the real data shows more scatter effects than the simulation. Note also that the real munition is partially filled with some material (water); it is not possible in this version of XRSIM to simulate more than one material in a radiograph. Finally, more detail appears to be at the top of the real munition compared to the top of the simulation; this is because there is no lid on the simulated object, and the tube (burster well) does not fit in the collar in the real munition. These are encouraging images, and similar simulations will be used in the design of radiography and CT systems for munitions inspection.

In Figure 5, a comparison is made between an image simulated with MCNP and a real image. Again the object is a munition; the object is tilted to simulate the imaging of the liquid level in a partially filled munition. In this case only a part of the munition is imaged. The simulation took a few hours to set up and around 50 hours (200 MHz Pentium Pro) to calculate; the image is the result of throwing 30-million photons. Though this is a fairly simple object (and it took a long time to simulate), the figure shows in a proof-of-principle sense that we can simulate imaging with MCNP.

Summary. In this task a survey of available x-ray-imaging simulation programs was performed and three programs were brought in and evaluated. This evaluation is summarized in Table 1. A capability to simulate systems similar to those in our lab has been demonstrated. Other groups at the INEEL have shown interest in this simulation capability.

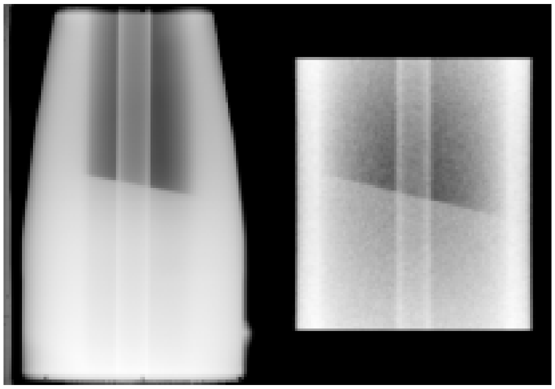

Figure 5. Radiograph of actual munition with a-Si detector (left) and simulated with MCNP (right).

Table 1. Summary of simulation programs reviewed.

	MCNP	XRSIM	MIRL Package	HADES[a]
Source	LANL	CNDE at ISU	MIRL at UU	LLNL
Type of simulation	Monte Carlo	ray trace	ray trace	ray trace
Scatter	yes	Poor	no	unclear
Beam hardening	yes	Yes	no	yes
Ease of use	Very complicated	Very easy	complicated	unclear
Speed[b]	Extremely slow (60-hrs)	Reasonable (20-60-sec)	Reasonable (60-120-sec)	unclear
Comments	Very accurate results, painful to use. Good for single radiographs. Better for single-detector systems.	Simple to use. Does not simulate source spot size, detector resolution. 3D version may be better.	Good for generating multiple images for CT reconstruction. Good for investigating alignment issues.	

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[a] Code has not yet arrived; analysis based on code description/users manual.

[b] Estimated time to complete similar simulation for XRSIM and MCNP. Time to generate full CT data set for MIRL code.

We are still awaiting the arrival of a fourth piece of code, HADES, which will be compared with the other ray-tracing packages. We would also like to try to get the latest version of XRSIM which has an improved user interface (which would be important to RWMC) and an ability to simulate multiple materials (up to 5) in a single object. And, now that we know about some of the problems associated with imaging with MCNP, it is worth checking to see if it is possible to image more easily with other Monte Carlo packages. Every simulation program has its distinct capabilities and strengths, and all three programs will be used at the INEEL.

Environmental Modeling

Principal Investigator: Miles A. McQueen

Background. The purchase of the 40-node INEEL Beowulf system was held up until it was too late to acquire and install in FY-98. Consequently, we decided to proceed to meet our objectives by continuing to select a set of benchmarks for the Beowulf, but to run them on a very small, two-node cluster. This alternative plan still gave us the desired experience both with the benchmarks and the entire MPI, Fortran 77, and Linux development environment.

FY-98 Technical Accomplishments. Benchmarks to estimate performance come in a variety of types including application, kernel, toy, or synthetic. A large number of benchmarks are available in each of these categories. The criteria used to select our benchmarks included: they must have already been written using an MPI implementation, they must have results readily available from other systems so that we can eventually compare our performance and price/performance, they must be portable in a timely fashion, and they must be free. In an informal evaluation using these criteria the NPB kernel benchmarks were considered superior.

The primary benchmarks we chose to run on our two-node cluster was the Numerical Aerospace Simulation (NAS) Parallel Benchmarks (NPB) based on Fortran 77 and the MPI message passing standard. NPB was written and is currently administered by the NAS Facility. NPB consists of the eight kernels EP, MG, CG, FT, IS, LU, SP, and BT. As expressed in the NAS facility documentation "EP is an embarrassingly parallel benchmark that primarily computes random numbers and provides an estimate of the upper achievable "Mop/s." MG is a multigrid kernel that requires highly structured long distance communication and it tests short distance communication as well. CG is a kernel that implements a conjugate gradient method to compute an approximation to the smallest eigenvalue of a large, sparse, symmetric, positive definite matrix. It tests irregular long distance communication, employing unstructured matrix vector multiplication; FT solves a 3-D partial differential equation using FFTs. It is a rigorous test of long distance communication performance; IS is a large integer sort that is important in "particle method" codes. It tests both integer computation and communication performance; LU is a simulated computational fluid dynamics (CFD) application that uses symmetric successive over relaxation to solve a block lower triangular-block upper triangular system of equations resulting from an unfactored, implicit, finite difference discretization of the Navier-Stokes equations in three dimensions; SP and BT are simulated CFD applications that solve three sets of uncoupled systems of equations. These systems are scalar pentadiagonal in the SP code, and block tridiagonal with 5x5 blocks in the BT code.

The benchmarks CG, FT, MG, LU, and IS are optimized for a power of two processors so were eligible to be executed on the two nodes of our small cluster and may be executed on 32 of the processors in our Beowulf system when it becomes available. SP and BT are optimized for a square number of processors so would be run on 36 processors in the complete Beowulf system. EP could be executed on the two-node cluster or on all 40 nodes of the INEEL Beowulf. Unfortunately, EP returns a Mop/s value rather than the desired Mflop/s metric.

The NPB class A (small) version 2.3 of the benchmarks were used without modification to the source code. Make files and system parameters were modified as necessary to run the code on our particular two-node system. The two-node cluster is described and the Gflop/s rating for each successfully executed kernel are given below

Since neither the hardware nor software was immediately available within the INEEL, the initial small two-node cluster was built at home using personal resources. The cluster consisted of one 486 50 MHz node and one P75 node connected using a standard 10baseT interconnect. We attempted to add a PII node but ran into quite a few difficulties making Linux operational so the PII was set aside and never became part of the cluster. Each of the nodes ran Red Hat Linux 4.2 with NFS support installed. MPICH and the NPB2.3 benchmarks were downloaded, configured, and compiled. The first benchmark run was EP class A. This benchmark was run on each node individually and then on the nodes working as a cluster. The 486 node executes the EP code at only a quarter of the rate of the P75 so the benchmark ran slower on the cluster then it did on the single P75 machine. To complete execution of the EP benchmark, the 486 took 8,353.96 seconds; the P75 took 2,489.66 seconds; and the cluster took 4,141.13 seconds. A different allocation of computation is required in order to get improved performance from the two-node cluster.

Two other benchmarks were also successfully run on the two-node x86 cluster. The NPB benchmarks completed were CG and LU. They ran at 2.26 and 3.47 Mflops respectively. SP, MG, IS, BT, and FT were also run, but after days of computation, error messages were returned. After much troubleshooting it was discovered there was an incompatibility between the x86 machines, Linux 4.1, and MPICH.

Excluding the EP benchmark, the expected Gflop/s rating for these NPB benchmarks, running on the 40-node INEEL Beowulf, is expected to range between 0.5 and 2.0. The SpaSM molecular dynamics application that has been run on the LANL Beowulf is expected to yield a result of between 5 and 7 Gflop/s if run on the initial 40-node INEEL Beowulf.

Finally, in order to have an in-house testbed, Red Hat Linux 5.1 was ordered along with the necessary support hardware to build a two-node cluster at work using 100MHz and 166MHz Pentium computers. Despite a few software incompatibilities the work cluster is essentially operational. It will be the initial testbed for followon work to be performed in FY-99.

Beowulf Systems and Applications:

A search of the Internet and Beowulf mailing list archives yielded a list of over twenty Beowulf systems at laboratories and academic institutions. This number has been rapidly growing during the last quarter of FY-98. The number of nodes varied between four and one hundred and fourteen. The majority of systems use Pentium Pro or Pentium II processors, run the Linux operating system, use one of the MPI libraries, and use applications written in Fortran. In general, but certainly not exclusively, the nodes have been built by physics or other scientific groups within their respective institutions. There are a few locations where computer engineering and science issues are the primary focus of the Beowulf group. A short list of the systems and their (few) scientific applications was created. To do a complete survey, all other message passing computing systems should be searched and any applications using MPI or PVM should be listed independently of whether they are running on a Beowulf system. These systems would include the large multithousand-node systems being built under the ASCI umbrella. It was beyond the scope of this task to even attempt such a survey so the search was limited to just Beowulf type systems and scientific applications that might be of interest to scientists internal to the INEEL. It will be incumbent on individual scientists to search for their own specific application of interest and to port them onto the INEEL Beowulf when available.

Summary. Unfortunately, the purchase of the 40-node INEEL Beowulf system was significantly delayed so this task had to be modified as we proceeded. Experience was gained in parallel processing environments through the process of building a couple of small two-node clusters and configuring both hardware and software so they could run the selected NPB benchmarks. The process of building the software environments and running the benchmarks was very time consuming as well as instructive. Our efforts clearly demonstrated the difficulty of building the software environments for a variety of machines, hardware configurations, and software systems. This points out the efficacy of our rigorously copying the LANL Beowulf model in the purchase of our first Beowulf system.

The metrics gained through benchmarking the two-node cluster are not directly relevant to the 40-node INEEL Beowulf but were still valuable in pointing out the potential for significant load balancing problems in heterogeneous computing systems.

Developing EM Relevant Decision Support Systems for Evaluation of Environmental Systems

J. M. Beller, R. P. Breckenridge, S. J. Cherry, M. R. Jackson,
M. A. Manguba, and R. C. Rope

BACKGROUND. Definition of EM Requirements for Long-term Environmental Management—The complexity of environmental regulations, data, and systems interactions associated with environmental management at DOE facilities creates a maze that decisionmakers must navigate. Requirements driving the need for a decision support system (DSS) for management of environmental systems were identified from federal statutes and regulations, DOE's policy on ecosystem management, CERCLA records of decision (ROD), and the EM integration process that is developing "Paths to Closure" (DOE, 1998). These requirements clearly state that stakeholder input and sound science need to be used to define how land will be used, restored, and managed as open space over the next 100+ years (INEEL, 1997).

As a federal land manager, DOE is responsible for conserving fish, wildlife, and plant populations and their habitats on the INEEL. DOE-ID is also responsible for evaluating how cleanup, development and land preservation options are integrated into a long-term land management plan. The current DOE-ID priorities emphasize environmental remediation activities. However, there are also legal requirements for proper record keeping and the long-term management of environmental information. Special attention is being given to the core data sets needed to support the DSS and to maintenance of these data sets in a format that can be readily updated and remain accessible as technology advances. Based on this review and interviews conducted, the major areas that are in need of additional attention and that form the basis for development of a DSS (Figure 6) include the following:

Landscape-level Management—DOE does not have the authority to directly manage species, but they do manage actions and processes (i.e., EM Integration) that affect multiple species, habitat and ecosystems. Landscape-level issues are often overlooked because of the scale, size of data sets and complexity. There is a need to identify how advanced decisionmaking tools can be used and integrated using standard electronic format to help stakeholders address issues such as (1) fire management (and related impacts to protected biological and cultural resources), (2) revegetation practices and control of weeds, (3) landscape fragmentation, (4) wildlife and domestic livestock grazing, (5) road/railroad/utility corridor construction and set-asides, and (6) management of recreationally important species.

Integrated Water Management—The INEEL serves as an important area overlying the upper part of the Snake River aquifer. The sinks located on the INEEL also serve as a recharge area for the Big Lost and Little Lost Rivers. Extensive development of agricultural lands around the INEEL are changing how water is used and managed. There is a need to develop methods to address integrated management of these resources that consider how current and future land use on and around the INEEL will affect its surface and groundwater resources.

FY-98 Technical Accomplishments. Develop Contacts for Decision Support System—Numerous collaborative relationships were initiated with other DOE laboratories, federal agencies, and research investigators. Table 2 summarizes the most significant of these contacts where extensive interest was expressed by collaborators.

Conceptual Framework—The conceptual framework for the DSS has been developed to address program, policy, and regulatory requirements mentioned earlier. The conceptual framework is based on the Environmental Management Decision Support System Functional Requirements. This conceptual framework has two main functions: (1) identify the direct relationships between variables, (2) provide the means to identify simulations, models, and databases needed to understand the system aspects of land management decisions. In addition, it provides a means to determine the components that exist and others that still need to be developed.

The framework is divided into four major categories: ecology, water, socioeconomics, and air. These categories are further divided into subgroups for which specific outputs from the DSS will be provided. Breakdowns for the other categories are available in the project files. The framework consists of databases, models, and simulations that provide the information, analysis and representation of the results of the ecosystem being evaluated. As a change to the ecosystem is proposed, the DSS will take this change (input) and use the appropriate databases and models to analyze the effects. The simulation components present the results in a GIS or other graphic format.

The following example will help to better understand how the DSS will work.

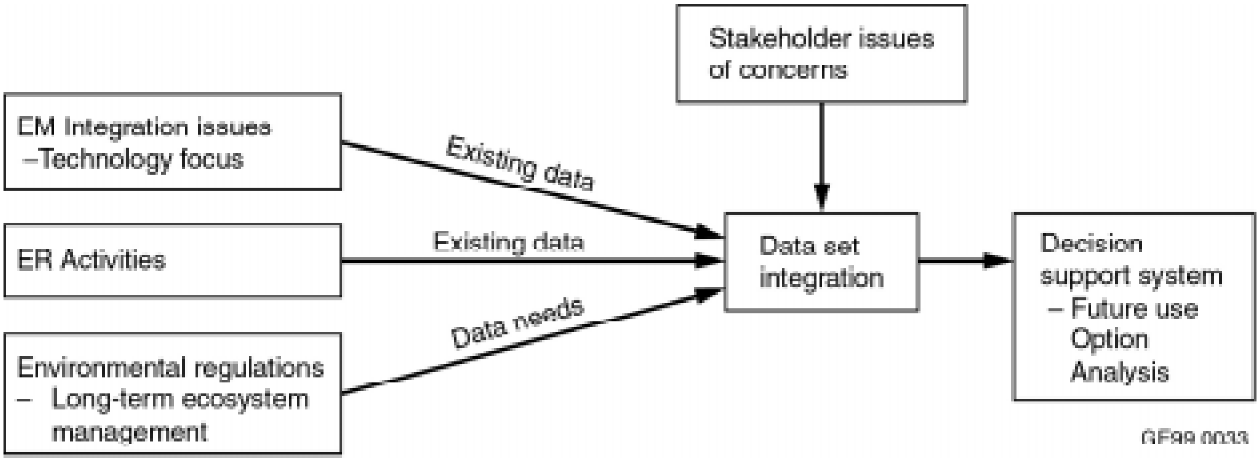

Figure 6. Linkage of current drivers to need for DSS.

Table 2. External list of collaborators.

Contact Point	Area for Collaboration
Jeffrey Holland, 601-634-2644, U.S. Army Corps of Engineers (USACE)	DOD is embarking on developing a land management system (LMS). This is a joint effort of four of the U.S. ACE labs. INEEL's activities related to the decision support system and uncertainty analysis as well as the web-based information server are components that are being discussed with DOD.
Mike Passmore, 601-634-4862, U. S. Army Corps of Engineers	Mike Passmore is developing an integrated bioeconomics planning system for cost-effective design of ecosystems. This is an ARCVIEW supported system with standard Windows features and is being used to address environmental and economic analysis associated with habitat change on DOD lands. INEEL's biotic database is being evaluated as a test case for this system.
John Hummel, 630-252-7189, Argonne National Laboratory	ANL is developing a dynamic environmental effects model (DEEM) which can be viewed at http://www.dis.anl.gov:80/DEEM/DEEM.homepage.html . This system is a dynamic model for evaluating interplay and feedback between different environmental factors. The systems is mostly being developed to look at impacts of mobilization of DOD forces, but has application on DOE lands relative to rapid changes of demographics or installation of a new facility. Discussion of using INEEL's change detection data with the DEEM are showing promise.
Oak Ridge National Laboratory	ORNL is developing the National Center for Environmental Decisionmaking Research. The mission of the Center is to improve environmental decisionmaking at the subnational level. Their website is http://www.ncedr.org. The Center has identified numerous tools useful in environmental decisionmaking. Collaboration with the Center on applying these tools to land management decisions has been discussed and is being pursued through our interlab agreement.

Table 2. (continued).

Scott Akenhead Facet International Scott_akenhead@bc.sympatico.ca	Facet is decision support system developer in the private sector, working with Southern California Edison on relicensing of some of the hydroelectric projects. Collaboration between the groups focuses on using their Java framework to develop three interactions for land management. This effort includes cascading analysis where land use changes in uplands can affect river models as well as biotic resource and contaminant transport. This provides a nice linkage between our DSS system and INEEL's visualization lab 3-D groundwater modeling effort.
John Davis, University of Bristol, U.K.	Collaboration on assembling uncertainty evidence for decisionmaking is being discussed. Use of the JUNIPER software developed by Dr. Davis for decisionmaking in the oil exploration field and applying the software to land management decisions will allow graphic representation of uncertainty associated with the data needed to support these decisions.

Question: *How much water from the Big Lost River is available for cooling a proposed fusion reactor?* In order to answer this question, we need to look at the availability of water during low precipitation years. Figure 7 represents the water category of the conceptual framework. The simulation S-4 provides the results of the question being asked. S-4 manipulates the results from the four directly linked models (M-7, M-8, M-9, and M-10) to determine the surface water flow within the watershed and displays these results in a GIS format providing a visualization of the flow throughout the watershed in a low precipitation year. In this case, we have defined the output of M-7 as our input to the DSS, a low precipitation year. The other simulations will provide the results of other indirect, but related issues resulting from a low precipitation year. These may include issues such as ecological impacts, impacts to recharge and flow of the aquifer, impacts to ground and surface water quality, and impacts to riparian areas.

Each of the four models that provide input into S-4 obtains information from other components in the framework. In our example, the irrigation model (M-9) requires information from S-8 (Land Use) and S-18 (Agriculture Economics). Changes in precipitation will affect land use decisions including what crops are planted. These effect the irrigation practices and the water available for flows down stream. Both S-8 and S-18 also require information inputs from other multiple components throughout the framework and provide inputs to other related components.

Trial DSS Software—Several categories of trial DSS software are being evaluated and are reported on in Table 3. These include:

- Software for manipulation of data to support land use change decision
- Software for conducting uncertainty analysis
- Integrated systems software.

Uncertainty Analysis—Uncertainty analysis is a critical component to developing a decision support system. If conducted appropriately, this analysis allows for sensitivity determination to be done to identify those parameters within a decision support system that have the greatest impact on the overall decisions. The decisionmaking process evaluates incoming information and its uncertainty and then looks at the outcomes together with the associated risk and opportunity. An important requirement of the DSS

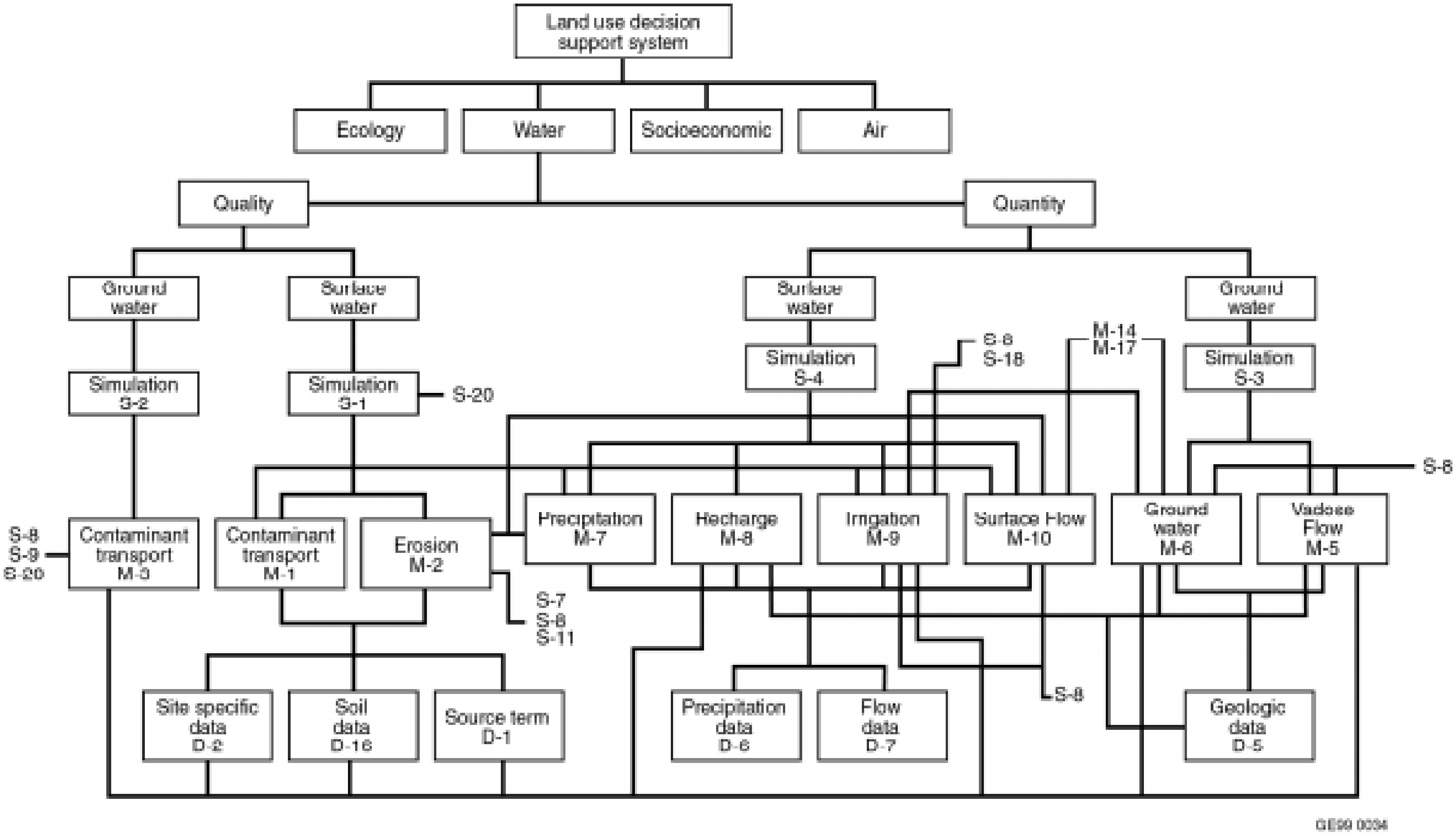

Figure 7. The water category of the conceptual framework for the DSS example.

Table 3. Application of software to support DSS.

Software	Capabilities	Area for Application
Change detection software for linking remote sensing imagery with geographic information systems (a co-funded effort)	An analysis of change detection for large remote lands such as DOE sites can be accomplished using Landsat Multi-Spectral Scanner (MSS) remote sensing imagery and integrating these using ERDAS IMAGINE, ARCINFO, and ARCVIEW software. These packages were tested to determine if they are useful in assessing change primarily on agricultural lands, but additional application for change due to fire, grazing, or land disturbance are also possible.	MSS scenes from July 16, 1973 and 1992 were obtained, registered, and rectified. Coverages were created in ArcView by manually digitizing polygons around the INEEL for agricultural lands using the 1973 scene. Coverages were then developed for 1992 and draped over the 1973 scene. Change detection analysis provides a strong tool for looking at changes due to disturbances over decades and provides a unique analysis tool for looking at change effects on future land decisions. For example, analysis of the area northeast of the INEEL around the Mud Lake analysis area in 1973 shows there were 28 center pivots. The same area in 1992 had 139 center pivots. In 1973, 448 acres were irrigated by center pivots and in 1992, this had increased to 2,240 acres. Overall water usage by center pivot systems (based on average rates) increased from approximately 3.3 million gallons per year in 1973 to 16.4 million gallons per year in 1992. Most of the new center pivots are fed by groundwater. This fourfold increase in water use by center pivot can be an important factor in transport of water and associated contaminants onto and across the INEEL.
JUNIPER	Uncertainty analysis software	This software provides graphical representation of the precision and accuracy of data available on different environmental components to assist decisionmaking. A decision tree is being developed of the relationships between the processes, similar to those identified in the conceptual model and uncertainty values associated with each of the decisions are being assessed based upon available data. Evaluation of the JUNIPER software should be completed in the early part of FY-99.
U.S. Army Corps of Engineers Land Management System (LMS)	Conjunctive water management modeling	Software requirements are just being developed for the USACE LMS. The Army Corps has substantial experience in surface water and groundwater hydrodynamics. The LMS direction is to link these components and develop a conjunctive water management model which is of high interest to DOE relative to land development around DOE facilities and its impact on contaminant transport and risk to ecological resources.

is that analysis of different future use options can be conducted. Uncertainty analysis is an ideal way to look at changes that different options will have to the overall decision process. The JUNIPER software is being evaluated for use in conducting uncertainty analysis in making decisions about INEEL future land management.

SUMMARY. The requirements for developing a decision support system for evaluating options for long-term management of DOE lands is a complex problem. The conceptual framework developed under this work identifies all major components of the environmental systems and is a critical piece of the decision support system. Another major piece under development looks at the uncertainty associated with various data and how they affect the outcome of the management option evaluation. Our approach of using uncertainty analysis in designing the decision support system merges information from data sources of known quality (i.e., field monitoring results) with simulation forecasts from models. A sensitivity analysis can then be performed on the known, simulated, and missing data to identify how the various pieces of information affect long-term land management decisions. Clearly, some information is more important and has greater potential to limit some future uses of land. Understanding these limitations and being able to evaluate the consequences of changing the influence of certain data sets makes it possible for decisionmakers to evaluate options, as well as evaluate the importance of specific data pieces. This will help focus decisions on data collection and modeling activities on those activities that provide the greatest return in the overall decision analysis process.

Future opportunities for using DSSs are tremendous given the advances that are being made in computational software, graphical displays, information feedback loops, and user-friendly platforms. The concept of a DSS that can provide stakeholders the ability to manipulate large data sets and models, graphically display results, and that is accessible through the Internet is close at hand. These systems must be validated on environmental decision scenarios (e.g., conjunctive management of surface and groundwater at a site or fire and habitat management), and the systems must involve and be supported by stakeholders. Once validated and accepted these systems can be used by DOE to manage its lands as valuable natural resources and integrate mission, economic, ecological, social and cultural factors into decisions that achieve comprehensive stewardship.

Summary of All Tasks

This program consists of four independent tasks. Each task was asked to establish environmental requirements in their technology area, identify sources within and without the DOE laboratories that could supply that software, obtain the software, and then perform some tests that would establish the applicability of the software to environmental programs. For the Decision Support System task, the requirements definition phase was expected to be more complex. Accordingly, that phase was scheduled to continue through August, and the subsequent phases are scheduled for the next fiscal year. With that exception, all the other tasks were scheduled to implement the software at the INEEL during this fiscal year. Even though the principal investigators were subject to receiving courtesy copies of the software from the other DOE laboratories, they were able to meet this aggressive schedule and obtain the excellent results that follow.

Implementation of the M2NOTS Code at the INEEL

The objectives of the project—(1) implementing the M2NOTS code at the INEEL, and (2) testing the code by comparing calculations with data for steam injection in fractured porous media experiments—were accomplished successfully. The comparisons indicate that the code needs to be modified to permit an increased number of nodes, especially if vesicular basalt that underlies the INEEL is to be modeled in the future. Other accomplishments of the project include:

1. Professor Kent Udell of the University of California at Berkeley presented a seminar and provided consultation to a number of INEEL personnel.

2. Interest was generated in the possibility of using the Steam Enhanced Extraction process for removing TCE contaminants at the TAN injection well. Professor Udell agreed to provide Robert Starr of the INEEL a "white paper" outlining the suitability of the method for the site and an estimate of energy, cost, and time requirements. A more extensive investigation of TCE cleanup using SEE would involve M2NOTS modeling of the TAN vadose zone.

3. Glenn McCreery, Kent Udell, and his graduate students agreed to pursue writing a conference paper on the comparisons of code calculations with experiments.

NDE Simulation

In this task a survey of available x-ray-imaging simulation programs was performed and three programs were brought in and evaluated. This evaluation is summarized in Table 3. A capability to simulate systems similar to those in our lab has been demonstrated. Other groups at the INEEL have shown interest in this simulation capability.

We are still awaiting the arrival of a fourth piece of code, HADES, that will be compared with the other ray-tracing packages. We would also like to try to get the latest version of XRSIM which has an improved user interface (which would be important to RWMC) and an ability to simulate multiple materials (up to five) in a single object. And, now that we know about some of the problems associated with imaging with MCNP, it is worth checking to see if it is possible to image more easily with other Monte Carlo packages. Every simulation program has its distinct capabilities and strengths, and all three programs will be used at the INEEL.

Environmental Modeling

Unfortunately, the purchase of the 40-node INEEL Beowulf system was significantly delayed so this task had to be modified as we proceeded. Experience was gained in parallel processing environments through the process of building a couple of small two-node clusters and configuring both hardware and software so they could run the selected NPB benchmarks. The process of building the software environments and running the benchmarks was very time consuming as well as instructive. Our efforts clearly demonstrated the difficulty of building the software environments for a variety of machines, hardware configurations, and software systems. This points out the efficacy of our rigorously copying the LANL Beowulf model in the purchase of our first Beowulf system.

The metrics gained through benchmarking the two-node cluster are not directly relevant to the 40-node INEEL Beowulf but were still valuable in pointing out the potential for significant load balancing problems in heterogeneous computing systems.

Developing EM-Relevant Decision Support Systems for Evaluation of Environmental Systems

The requirements for developing a decision support system for evaluating options for long-term management of DOE lands is a complex problem. The conceptual framework developed under this work identifies all major components of the environmental systems and is a critical piece of the decision support system. Another major piece under development looks at the uncertainty associated with various data and how they affect the outcome of the management option evaluation. Our approach of using uncertainty analysis in designing the decision support system merges information from data sources of known quality (i.e., field monitoring results) with simulation forecasts from models. A sensitivity analysis can then be performed on the known, simulated, and missing data to identify how the various pieces of information affect long-term land management decisions. Clearly, some information is more important and has greater potential to limit some future uses of land. Understanding these limitations and being able to evaluate the consequences of changing the influence of certain data sets makes it possible for decisionmakers to evaluate options, as well as evaluate the importance of specific data pieces. This will help focus decisions on data collection and modeling activities on those activities that provide the greatest return in the overall decision analysis process.

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ISSUE ANALYSIS AND RESOLUTION THROUGHOUT THE DOE COMPLEX

B. Kaplan

Scope and Objectives

This effort is to develop methods for unbiased assessment and resolution of issues facing DOE-EM. It is to identify and resolve significant roadblocks preventing solution to complex-wide EM issues. It seeks to identify a set of EM issues relating to INEEL Core capabilities, and roadblocks that could have a long-term impact on our ability to produce system-wide solutions for EM.

For FY-98, the following project activities were planned:

- Review literature concerning neutral facilitation, arbitration, and honest brokerage theory and practice.
- Review public information about structures and practices of organizations that consider themselves honest brokers.
- Review issues and problems facing DOE and INEEL that may require honest broker assistance for successful completion.
- Select best practices of organizations that are considered exemplary in carrying out honest broker functions.
- Develop a definition and theory of honest brokering that can guide the development of capabilities for honest brokering at the INEEL.

Technical Accomplishments

Background

Preliminary review of the literature, and review of ongoing projects determined the concept of an honest broker is at the heart of providing a complex-wide issue analysis, and managing organizational conflict of interest. This workscope specifically addresses what it takes for INEEL to successfully perform its role as an honest broker, or successfully take advantage of outside resources in this area. The generally accepted definition of an honest broker is a neutral agent, who acts as a mediator, facilitator, and/or arbitrator with close adherence to a moral or ethical code. The broker deals fairly, candidly and impartially with all parties and provides a forum for the participants to understand and evaluate choices available to them. An honest broker enables groups to be more effective in doing collaborative work.

The need for an honest broker for complex-wide issue analysis, and managing organizational complex of interest arises whenever there are diverse groups with differing agendas working on technically or politically complex problems that have no simple solutions. The need for an honest broker also arises when the problems address national needs or (in the Department of Energy) complex-wide issues. In problems of this type, vested interests or personal agendas can cause wrong paths to a solution to be taken. In these cases, there is a need for a neutral agent to promote, guide, and safeguard the process of negotiation and discussion itself. The process becomes the means by which all sides are heard and mutually satisfactory solutions can often be found. The honest broker, then, is the guardian of the process, rather than of any position or point of view.

Issues that are important to the Department of Energy (DOE) mission often have global or complex-wide scope. For this reason, officials from DOE, their supporting research laboratories, and additional regulatory and advisory agencies have often found it difficult to agree upon necessary goals and meet necessary task demands. The complexities of the various levels of communication, and the highly technical information that is involves, make it difficult to understand the complex decisions and issues that surround those decisions. The challenge for the honest broker is to first identify the specific issues and challenges being faced, and then to assure that the appropriate knowledge and skills are effectively brought to bear to address them.

The benefits of the improved honest brokering capabilities should include better inter-agency decisionmaking for the DOE, regulators, stakeholders, environmental contractors, and the public. The results of using these capabilities are as follows:

- Faster approval of technical reports and documents
- Easier to implement consultation and collaborative processes in accordance with regulatory agreements
- Assist all parties in sharing information and working collaboratively to define and implement solutions
- Encouraged participation and build internal commitment by affected parties
- Assists parties in meeting and/or exceeding organizational or programmatic goals
- Develop more effective strategies, and better assure successful implementation
- Develop innovative approaches to improving cost-effectiveness, greater efficiency or more advanced techniques and solutions.
- Assist with trust building and opening communications
- Assist with increasing or enhancing decisionmaking skills in others
- Assist with the development of teams that can work together
- Assist with determining commonalties and differences and seeking resolutions based on these.

This workscope is also responsive to the joint issued joint guidance by DOE and EPA: “Improving Communications to Achieve Collaborative Decisionmaking at Department of Energy Sites (June, 1997).” This guidance encouraged the use of collaborative decisionmaking. Examples of savings when these techniques were used included:

- $270 million cost avoidance at the Hanford Site by improving methods for meeting remedial action objectives and focusing resources on technical needs and not quotas. (Reference: “Collaborative Decisionmaking Between Federal and State Agencies Yield Cost Savings of Approximately $275 Million,” March 1998).

- $160 million cost avoidance at Oak Ridge the Oak Ridge Site by refining risk numbers. (Reference: "Collaborative Decisionmaking in Cleanup at DOE Site," Federal Facilities Environmental Journal, Autumn 1997)

- $14 million cost avoidance at the Mound Site by modifying the CERCLA operable unit approach. (Reference: above)

It is toward the generation of success stories such as these that this workscope is aimed.

FY 1998 Accomplishments

The accomplishments associated with the work are best described in terms of two spaces, the problem space and the solution Space. Issues in the problem space range from those that are very high level, including national or global problems which the DOE may be chartered to address, to complex-wide problems for the DOE system as a whole to address, to site-specific problems, including those faced here at the INEEL. For the purpose of this work scope, we have been interested in seeing where and how issues, at all these levels in the problem space, might benefit from improved methods of complex-wide issue analysis, managing organizational conflicts of interest, and the help of an honest broker to bring all this about. Similarly, in the "solution space," are the problems and issues one would face in actually doing a complex-wide issue analysis, or performing the work of an honest broker. We have tried to identify these issues as well. There are issues of both types in this report.

The following are the Issues and problems that have been identified though in-depth work with the Mixed Wasted Focus Area, the Biotechnology Programs, The Decisionmakers' Forum, as well as more conceptual work. Some of these issues have come with suggested solutions, which are being taken as hypotheses to be tested through literature review and field work. The issues below are grouped into these sets.

Problem Space

Complex-Wide Issues.

Issue: Implementing Technology Generated at the National Laboratories

The Laboratories are very efficient at developing or inventing technology, but not necessarily in implementing this technology. A contributing factor is their need to deal with diverse group of stakeholders.

For example, software has been developed that has the potential to design nuclear fuel cores that are safer. To implement this software for relicensing nuclear cores it will take a diverse group of stakeholders. The regulators will have to be confident that the software and analysis techniques produce safer cores. The nuclear plant owners will have to be confident that the new software will result in nuclear cores that are more efficient and produce higher output. And so on for the fuel manufactures, engineers who do this analysis, others. To develop techniques that are acceptable this diverse group of stakeholders must reach a shared perspective regarding what pilot study is needed to resolve these concerns. When the group is brought together there are issues that can best be addressed by an honest broker. Examples of such issues would include: how can the regulator and regulated can legally work together, how to efficiently develop the technology, how to manage conflict over competition and conflict of interest issues.

Representatives for the honest broker team met with INEEL staff that believe the technology is now available to streamline the core analysis and licensing for commercial nuclear reactor cores. These techniques can produce safer and more efficient plants. Safety and regulatory burden reduction should be attractive to the regulators. Efficiency equates to more power and large savings for plant owners and consumers.

Issue or Problem: Mediate to Solve Conflict Between Organizations in DOE or Other Government Agencies

The Committee on Remediation of Buried and Tank Wastes of the National Research Council has been in existence since early 1993 to provide scientific and technical oversight and evaluation of the U.S. DOE Office of Environmental Restoration (EM-40) program of remediation activities with the Defense Nuclear Waste Complex contaminated with radioactive and mixed wastes. The committee has observed a lack of sufficient progress toward DOE's remediation goals, and has observed inefficiency. The committee has been searching for the causes of the lack of progress in environmental remediation. In searching for the causes the committee identified seven symptoms that contribute to this lack of progress. Symptom 6 deals an aspect where honest brokering could help. General Symptom 6 is called "A lack of Organizational Coordination." This lack of coordination is between DOE's Office of Waste Management (EM-30) and DOE's Office of Environmental Restoration (EM 40). The report states that these Offices must rely on Memorandum of Understanding (MOUs) to try and get things done. The fact that the subunits in these Offices must use MOUs "reflects deep organizational problems." Honest brokering techniques could be provided to alleviate these organization difficulties by providing third party mediation for these offices.

Another problem identified in this study was "facility transition, deactivation and decommissioning cannot be done in a vacuum, but must be done in light of standards for cleanup and future land uses." An honest broker could be brought in to facilitate the group and individual interaction processes necessary to gain stakeholder consent. (Reference: Barriers to Science, Technical Management of the Department of Energy Environmental Remediation Program, National Research Council, 1996)

Organization barriers have been observed in other government agencies that have regulatory roles. For example, conflicts have been observed between branches in the Nuclear Regulatory Commission that cause inefficient use of resources. An honest broker could serve the role of a third party mediator, and clear the roadblocks caused by this organizational difficulty.

Issue: Need for Collaborative Decisionmaking at DOE Sites

EM recently issued the final guidance on "Improving Communications to Achieve Collaborative Decisionmaking at Department of Energy Sites" dated June 16, 1998. This guidance was developed by a joint effort by the DOE and EPA with substantive input from State regulators. The guidance document list several factors that led to the development of this guidance. First, independent observers highlighted the need for improved communications both within, and between organizations in DOE. Second, given increasing fiscal constraints, regulators are playing a greater role in budget planning in DOE. Finally, DOE must identify the necessary work that will be undertaken to achieve the most suitable remedy. Identifying this work would require greater work with stakeholders to determine what a suitable remedy will be. Identifying an agreeable remedy that has the consent of stakeholders would save money, focus effort on the appropriate actions, and accelerate cleanup.

DOE says that improving communications is critical to achieving the DOE's goal of completing cleanup at most sites within a decade.

Issues Related to Work with the Mixed Waste Focus Area.

Issue: DOE and EPA Collaboration for Standards Development on Leeching

Honest broker team members have been working with members of the Mixed Waste Focus Area to facilitate development of a new mixed waste leeching standard. This standard will be developed by a joint EPA-DOE, and possibly NRC, committee. A standards organization such as American Society of Mechanical Engineers may be involved because of the expertise in developing standards.

There are several roles for an honest broker in this project. First this is a new endeavor that should be carefully planned if it is to succeed. One observed problem is inefficient standards development. It is not unusual for a standard to take 10 years. Using efficient meeting techniques (reference electronic meetings) it should be possible to shorten this time. A third party to assure contributors are held accountable for milestones and deliverables should speed this process and insure efficient exchange of information such as meeting minutes.

Because we are dealing with multiple agencies, it is likely that organization conflicts to arise. Mediation between the EPA, DOE, NRC, public, and other stakeholders may be necessary. Unless careful consideration of issues that can arise by an honest broker, the process my not succeed. Having an independent third party honest broker may eliminate perceived agency biases. For example if a DOE technical representative were to chair the effort, EPA may consider the resulting standard as slanted toward facilities.

There are also group and individual relational dispute resolution techniques that should be applied by an honest broker to aid in efficient meeting development.

Representatives for the honest broker study team have met with representatives from the Mixed Waste Focus Area to determine ways to proceed. We have proposed that INEL develop a joint standard with DOE and EPA. We proposed using a standards organization such as the American Society of Mechanical Engineers that is in the business of writing standards. We learned of a Public Law that requires federal agencies to use industry consensus standards when possible. ASME has the ability to bring a diverse group of stakeholders to the table to develop a standard that is workable. We believe that we can add value and speed this process using new group facilitation processes.

This suggested approach should be in accordance with the “Final Guidance on Improving Communications to Achieve Collaborative Decisionmaking at Department of Energy Sites” jointly developed by the EPA and DOE.

Issues Related to Biotechnology.

Issue: Implementing Environmental Biotechnology Complex-wide

The country and the DOE suffer from a lack of direction, issue prioritization, and sense of urgency related to the efficient use of Environmental Biotechnology to solve major cleanup problems.

For example, pharmaceutical support of biotechnology for creating medicines is impressive. However, the use of environmental biotechnology to safely and efficiently enhance cleanup suffers from a lack of government policy and planning. A national biotechnology forum similar to the Domenici forum is needed to develop research and policy for all of the U.S. The output of this forum would be to identify issues, needs and funding for biotechnology. The breadth of the meeting would be large ranging from the use of phytology to support remediation to evaluating why food safety in this country in the presence of E coli outbreak does not include the use of gamma radiation. Technology roadmapping, alignment with agricultural programs, and national U.S. participation help comprise some of the problem space in this area. To reach aggregate consensus on issues, technologies, and priorities will take brokering a diverse group of stakeholders including government agency representatives, university, and national laboratory staff. The complexity regarding the problem, technologies involved, number of stakeholders, and national importance/urgency and the potential for multiple agency self -interest suggest that honest brokering be employed in order to prevent rational resolution and policy from being compromised by parochial interests.

Using the Decisionmakers' Forum as a model, the INEEL can design and implement such a meeting that would serve a national need.

Issue: Facilitate the BIC in order to reduce Conflict between National Laboratory Organizations in the Area of Environmental Biotechnology

The honest brokering consultancy is working with Lamar Johnson, Biological Sciences who will become the president-elect of the Biological Research Coordination Group (BIC). The BIC is an inter-laboratory group made up of DOE laboratory representatives. The committee in recent times has failed to make sufficient progress in terms of identifying actions, objectives, and initiatives. In particular, one of the goals beyond generating face-to-face honest communication between the participants will be to keep representatives of the BIC in contact with one another in order that meetings can be more productive from DOE's standpoint and the standpoint of the individual national laboratories sending high-level attendees to the meetings." The group will be assisted by technologies used to support meetings and facilitate the decisionmaking processes that are available to the honest brokering consultancy. The BIC will be able to better focus and take on challenges related to making more prominent the role of the biological sciences in supporting DOE's Office of Waste Management (EM-30), DOE's Office of Environmental Restoration (EM 40), and EM-75. Barriers to date have resulted not so much from each laboratory's internal organizational barriers but from commitments of BIC attendees to support their own home organizations on various projects. Designing a clear direction, mission, vision, and objectives can accomplish a lot in making the BIC a more productive and influential organization.

Issue or Problem: LDRD Enterprise Development in the Area of Environmental Biotechnology

Honest broker team members have been working with members of the biological sciences group (Melinda Hamilton) and systems engineers to facilitate development of an enterprise proposal that would help INEEL to become state of the art and to make a national contribution in the area of microbial sciences. Honest brokering will be used to assist in the data collection and workshop phases of proposal development. The final product will require input from a variety of stakeholders including diverse groups within the INEEL, university experts, and industrial representatives. The product will also be designed to existing requirements and will support long-term laboratory business plan objectives.

There are several roles for an honest broker in this project. First, is helping biotechnology to identify all the parties that might be impacted or wish to play a role in this research. Next is to design data collection and or meetings that may be used to help move the proposal in the direction of supporting INEEL scientific leadership staff, research objectives, etc. By collaborating with the client it will be possible to identify multiple stakeholders, technologies, timeframes, and priorities and to ensure that there is a long-term benefit to the laboratory that exceeds just winning the proposal effort. The goal of honest brokering in this regard is to prepare for the future of biotechnology and enhancing the LDRD investment process. The honest brokering consultancy has a commitment to enhancing the proposal and this process and is neutral regarding the selection of one technical approach over another or the success of one INEEL group at the expense of another.

Conceptual and Cross-Cutting Issues

Issue: Problems in Stakeholder Communications

Dealing with external stakeholders can be difficult. Communications must be carefully planned to assure that all stakeholder input is obtained and project plans incorporate stakeholder input. Incorporating stakeholder input is difficult because of the issue of trying to meet the needs of all the diverse parties. Some stakeholders must be willing to accept solutions that are less than optimum.

Communication of these less than optimum solutions is critical to the acceptance of projects. In studies it has been found that the public will go along with projects that they do not believe is their best interest if several criteria are met:

- A serious problem or opportunity must be addressed
- The agency or person addressing the problem or issue is the right entity
- Not addressing the issue would be irresponsible
- The approach used is reasonable, sensible, and responsible
- The public believes people are listening to their concerns.

It is difficult to communicate these four items to a group of diverse stakeholders and in fact the communications has to be planned very carefully. Failing to communicate properly can result is organized and vicious opposition.

Possible solution**:** A technique has been developed to effectively communicate with a diverse group of stakeholders. The technique involves identifying the affected stakeholders, determining their interest, gaining their input, and incorporating their concerns into project plans. These concepts are applicable to a city planning project or to a DOE cleanup project.

Issues Regarding Mediator Resources Ethical Standards

The model standards for mediators, endorsed by the American Bar Association, Society of Professionals in Dispute Resolution and American Arbitration Association poses several issues for the INEEL Honest Broker Project. One aspect that we have found for honest brokers is the role of neutral mediator. Thus, we feel that these values raise issues that we must face and resolve.

Standard 1—“self-determination: A mediator shall recognize that mediation is based on the principle of self-determination by the parties.”

Issue: As a subcontractor, it is entirely possible to be asked to facilitate a meeting in which the customer wants participants to be persuaded of a preconceived point-of-view or position. Since the mediation and facilitation process relies on the ability of parties to reach a voluntary, freely chosen agreement, it is necessary that this standard be maintained to maintain credibility in the honest broker and in the honest broker process. Policies may be needed to help mediators determine when a customer is requiring that this standard be violated and, if the situation cannot be resolved, for withdrawal from the process in such cases.

Standard 2—"Impartiality: A mediator shall conduct the mediation in an impartial manner."

Issue: A mediator must not only *be* impartial, but must *appear* impartial. This may be a challenge when mediating between the DOE and outside parties, or even when mediating groups within the DOE complex. If a mediator finds that he/she is losing their impartiality (due to personalities or behavior of some participants, for example), the mediator should either resolve the situation, or withdraw, or ask to be replaced.

Standard 3—"Conflicts of interest: A mediator; shall disclose all actual and potential conflicts of interest reasonably known to the mediator. After disclosure, the mediator shall decline to mediate unless all parties choose to retain the mediator. The need to protect against conflicts of interest also governs conduct that occurs during and after the mediation."

Issue: Without the consent of all parties, a mediator shall not subsequently establish a professional relationship in a related matter, or in an unrelated matter under circumstances that would raise legitimate questions about the integrity of the mediation process. A mediator shall avoid conflicts of interest in recommending the services of other professionals. . . . there may be strong pressures on the mediator to settle a particular case or cases. The mediator's commitment must be to the parties and the process.

Standard 4—"Competence: A mediator shall mediate only when the mediator has the necessary qualifications to satisfy the reasonable expectations of the parties."

Issue: This standard should refer to both training and experience in mediation and to technical competence in the subjects of mediation. Where honest brokers do not have the appropriate combination of facilitation/mediation skills and technical skills, they should call for outside help from someone who has the appropriate skills.

Standard 5—"Confidentiality: A mediator shall maintain the reasonable expectations of the parties with regard to confidentiality."

Issue: Since the parties' expectations regarding confidentiality are important, the mediator should discuss these expectations with the parties. If the mediator holds private sessions with a party, the nature of these sessions with regard to confidentiality should be discussed prior to undertaking such sessions. This may be a challenge to us, since it must be balanced against the need for an appearance of impartiality and open government (in some cases).

Standard 6—"Quality of the process: A mediator shall conduct the mediation fairly, diligently, and in a manner consistent with the principal of self-determination by the parties."

Issues: The honest broker will need to work to ensure a quality process and to encourage mutual respect among the parties. A quality process requires a commitment by the mediator/facilitator to diligence and procedural fairness, with adequate opportunity for each party to participate in the discussions. One should only agree to act as an honest broker when one is prepared to commit the attention essential to an effective process. One comment to this standard points out that, "Mixing the role of a mediator and the role of a professional advising a client is problematic, and mediators should strive to distinguish between the roles." This comment goes on to point out that the mediator/facilitator should recommend that the parties seek expert advise, providing sources to locate list of those giving such advice, rather than making specific recommendations.

Standard 9—"Obligations to the mediation process: mediators have a duty to improve the practice of mediation."

Issue: Mediators are regarded as knowledgeable in the process of mediation. They have an obligation to use their knowledge to help educate the public about mediation; to make mediation accessible to those who would like to use it; to correct abuses; and to improve their professional skills and abilities.

The challenge here, is to implement these ideals, rather than give lip service. Implementation will include continued measurement and feedback from clients about how we are doing, continuing education in mediation and facilitation techniques, and the willingness to stand up to our colleagues when, or if, they are violating these standards and to ask them to excuse themselves and, if they do not, see that they are removed.

Solution Space

Decisionmaker's Forum Process Critical Success Factors. On June 19, 1998, a Decisionmaker's Forum on a New Paradigm for Nuclear Energy (DMF) was held in Washington, DC. Approximately 60 nuclear energy experts from industry, academia, and government were involved in the Forum. Senator Pete V. Domenici, United States Senator from New Mexico was the sponsor for the Forum. The INEEL served as the host for the event, handling all of the arrangements, logistics forum design, facilitation, and followup.

The forum started with a plenary session where Senator Domenici, Representative Joe Knollenberg (Michigan) from the House of Representatives and several other individuals from the NRC and DOE addressed all participants. Shortly following the combined plenary session participants separated into three facilitated group sessions, with approximately 20 participants in each group. The groups addressed predetermined topics for "creating a new paradigm for nuclear energy." Each session lasted about five hours following a very prescriptive agenda and process. The three topic areas were Revitalizing Nuclear Energy, Global Nuclear Materials Management, and Advanced Nuclear Systems and Fuel Cycles.

A unique element of this forum was the use of electronic meeting hardware and software to get maximum input from forum participants and facilitate the forum outcomes/products. The process that was utilized during the forum greatly contributed to the overall forum success and the quality of the information gathered from this unique group of recognized nuclear experts

After the DMF, the forum record (electronic input from all participants) was reviewed and analyzed. A team of writers completed a DMF report containing 10 recommendations and the associated critical considerations. This report has since been passed on to Senator Domenici and his staff for followup actions.

The forum design team requested specific feedback (regarding critical success factors and lessons learned) from the participants and the Senator Domenici's office in Washington DC. Additionally, the forum designers/facilitators met to discuss lessons learned and critical success factors that could be captured for future use during similar events.

Facilitators and session leaders played key roles in accomplishing the desired outcomes of the forum. Listed below are five critical success factors that contributed to the overall success of this event, and from which lessons can be learned for similar events where honest-brokering (neutral facilitation) is utilized as part of an event or meeting design. These factors will not apply to all future designs; however they can be evaluated on their own merit for contributing to event success.

Conduct thorough and detailed process design planning well in advance of the event. Planning should include:

- Adequate time to complete and test the process design: The design team was given eight weeks to prepare for the event. The entire eight weeks was needed to refine the process and test assumptions regarding the specific approach. Multiple designs were evaluated and the best designs were tested for adequacy in helping to achieve the forum outcomes.

- A customer needs and requirements analysis: The design team had adequate time in defining the forum requirements. Defining who the ultimate customer early on in the process can alleviate ambiguity and second guessing later on.

- A deliberate audience analysis: A great deal of time was spent on audience analysis, who would be there, what agendas might they bring, what expectations would they have for the event, and how could we maximize the amount of information we captured from each individual.

- Identification of the right talent/capabilities to achieve the desired outcomes: The facilitators, group leaders, and technical support personnel were individuals with previous facilitation and process consultation experience. They were selected by the design team to facilitate the forum process design work and the event itself. Group leader selection was based on content expertise and ability to work closely in a dual meeting management role with the facilitator as the process guide. Since electronic meeting management software and hardware were utilized as part of the forum facilitation design, technical expertise (in-house and contract) was utilized to accommodate the need.

- Event design considerations, including meeting management technology considerations: Because of the short duration of time with the subject matter experts, electronic medium was used to capture the maximum amount of input in the shortest amount of time. In the future we would allow somewhat more time for open discussion and issue resolution. The opening plenary session was about 45 minutes long which compressed the rest of the day's schedule and forced curtailment of some of the planned discussion time in two of the three sessions.

- Consideration for process dry-runs or walk-throughs to validate the process before the event: Dry runs are a must to checkout process assumptions and techniques.

- A thorough potential problem analysis (PPA) and associated mitigating factors: We were able to avoid many possible problems due to a complete PPA conducted three weeks prior to the event.

- An event-specific strategy for facilitation and participant management: Many of the elements from the PPA focused on participant management. The facilitators were able to script-specific responses based on the mitigating elements in the PPA. The responses were utilized multiple times during the forum.

- A complete understanding of roles, responsibilities and expectations and negotiate specific contracts with key people involved in the process: The contracts should be in place for the entire duration of the event/meeting.

- Articulation of event outcomes and maintain focus on the outcomes during the planning phase and during the actual event.

- Allow enough time in the process for adequate discussion and issue resolution to encourage an appropriate level of commitment and ownership for the products of the event.

- Sponsorship and leadership at a high enough level to encourage involvement and commitment to participate and give meaningful input to the overall effort.

Types of Honest Broker Organizations. A number of organizations advertise themselves as honest brokers. They range from the National Academy of Science (which was set up, by law, to be an honest broker) through professional standards and research groups, to profit-making consultants who advertise themselves to be honest brokers. The types of honest brokering organizations follow:

The National Academy of Science—This is the exemplar. Mandated by Congress in 1863, the charter of the National Academy was, "… the Academy shall, whenever called upon by any department of the Government, investigate, examine, experiment, and report upon any subject of science or art …." This nonprofit organization provides a public service by working outside of the framework of government to ensure independent advice on matters of science, technology, and medicine.

The National Academy has carefully developed a set of safeguards to ensure their independence and impartiality that has served as the model for most other organizations doing this type of work. These safeguards are:

- Study committees are formed of well known and respected experts in each area

- Oversight and report review by supervisory boards and commissions who are stewards of the process

- Anonymous outside review of research reports to ensure that findings are fully supported by the evidence given

- Committee members are examined for potential conflicts of interest

- Do no research themselves, interview spectrum of informed parties and researchers, and review research literature, for each given question

- Mediation and arbitration occur within committees (building consensus and reconciling conflicting points of view) and in public meetings and for a being sponsored by the Academy.

With this model, then, we can review other organizations regarding how well they fit this model.

Professional Societies—Among the largest and best-known professional societies are the Institute of Electrical and Electronic Engineers (IEEE). The IEEE committee facilitators take on a brokering role when facilitating a consensus report. They broker the interests of each participant, ensuring all are heard. They facilitate the development of a consensus document, which is voted on by the IEEE committee. They address all concerns, both negative and positive, and if un-addressable, state why they were un-addressable. Every participant is accounted for, and their efforts documented. This includes those in favor, in favor with comments, and dissents.

Other examples of professional societies that play honest broker roles include the American Society of Mechanical Engineers (ASME), the American Institute of Chemical Engineers (AIChE), and the Society of Automotive Engineers (SAE). All of these organizations set standards for their respective industries, but only the ASME and AIChE also sponsor and perform research directly for their industries.

The standards committee process is similar for all these organizations. It is basically the same as the National Academy process for study committees in all respects except for anonymous outside review. Instead, review is by a large group of interested industry representatives who are known and whose objections must be addressed and resolved (with stated exceptions that are part of the process).

Test and Evaluation Organizations—The Consumer's Union and Underwriter's Laboratory (UL) may be the best known of these organizations. Neither of them fit the National Academy model, since they simply test to see whether certain products meet predetermined standards and do no negotiation, mediation, or arbitration.

Public Information Organizations—Nonprofessional organizations that are dedicated to the political and policy area are probably exemplified by the League of Women Voters and the Smart Voter Project. In these cases, the primary duty of the organization is to be stewards of the process, that is, to provide an open forum that tries to ensure that biases and partiality are known, while providing a chance for all sides to be heard. The committees are not selected to be unbiased, but are, rather, representative of the various biases that exist. The moderator from the organization facilitates, but does not mediate or arbitrate. Sponsoring these public forums is only one of the activities that these organizations pursue.

Facilitation Organizations—These organizations range from profit-making, like the Battle Arlington Office to nonprofit, like Northwest Regional Facilitators. These organizations are dedicated solely to the *process* of facilitation, mediation, and/or arbitration. Their purpose is to provide unbiased mediators/facilitators and, where the National Academy provides subject-matter experts in the topic of discussion, who are usually (but not always) skilled facilitators, these organizations provide skilled and experienced facilitators who may or may not be well-informed about the topics of discussion.

Reference

H. Bleiker and A. Bleiker, "Citizen Participation Handbook, For Public Officials, and Other Professionals Serving the Public," Tenth Edition, 1997.

Summary

This workscope has identified significant roadblocks preventing solution to complex-wide EM issues, and explored methods for their unbiased assessment and resolution. This workscope has also identified a set of EM issues relating to INEEL Core capabilities, and roadblocks that could have a long-term impact on our ability to produce system-wide solutions for EM.

To carry out this workscope, the following project activities were completed:

- Reviewed literature concerning neutral facilitation, arbitration, and honest brokerage theory and practice

- Reviewed public information about structures and practices of organizations that consider themselves honest brokers

- Reviewed issues and problems facing DOE and INEEL that may require honest broker assistance for successful completion

- Selected best practices of organizations that are considered exemplary in carrying out honest broker functions

- Developed a definition and theory of honest brokering that can guide the development of capabilities for honest brokering at the INEEL.

- Results of this work were captured as insights into problem space and solution space. Together, these insights have given us a better picture of the needs, the challenges, and the competencies required to address them.

INSTITUTIONAL PLAN AND BOARD OF VISITORS

FY 1998 Accomplishments

INEEL Institutional Plan

A draft Institutional Plan was written, reviewed by LMITCO senior management, and submitted to DOE for internal review and comment on July 7, 1997. This draft was posted on the DOE-ER server. The objective for FY-98 was to finalize the draft. The comment period concluded concurrent with receiving guidance for the FY 99-03 Plan. Format changes and additional required information were accomplished together with integrating figures and graphics in September and the document is now ready for management review. However, a revised long-range plan is imminent and modifications may be required for consistency.

Board of Visitors

On April 5–7, 1998, Dr. Bart Krawetz, Director of the INEEL, convened a meeting of a Board of Visitors in order to review the INEEL's long-range plans, business objectives, and strategies. The Board was comprised of a diverse group of nationally known technical experts, business executives, and academics (see Table 1). Dr. Edgar Berkey, Vice President and Chief Science Officer of Concurrent Technologies Corporation, served as Chairman of the board. A final report on this meeting was transmitted to Dr. Krawetz on June 29, 1998, and subsequently distributed to selected LMITCO management and upper management at DOE-ID.

Table 1. Members of the Board of Visitors.

Dr. Edgar Berkey, Chairman
  Vice President and Chief Science Officer
  Concurrent Technologies Corporation
  Pittsburgh, PA

Dr. Philip Brodsky
  Vice President, Corporate Research
  Monsanto Company
  Saint Louis, MO

Dr. Tuncer Cebeci
  MDC Distinguished Fellow
  The Boeing Company
  Long Beach, CA

Dr. Patrick Dugan
  Consultant
  Bioprocessing
  North Fort Myers, FL

Dr. Merton Flemings
  Toyota Professor of Materials Processing
  MIT
  Cambridge, MA

Dr. Norman Gjostien
  Retired
  Ford Research Laboratory
  Dearborn, MI

Table 1. (continued).

Dr. Charles Kolb
President and CEO
Aerodyne Research, Inc.
Billerica, MA

Dr. Victor Lechtenberg
Dean of Agriculture
Purdue University
Lafayette, IN

Dr. David Litster
Vice President for Research
MIT
Cambridge, MA

Dr. David McNelis
Director, Environmental Research
University of North Carolina
Chapel Hill, NC

Dr. Brian Pitcher
Provost
University of Idaho
Moscow, ID

Dr. Joseph Spencer
Director
South Carolina Universities Research and Education Foundation
Aiken, SC

Mr. Paul Williamson
Director of Programs
Lockheed Advanced Technology Center
Palo Alto, CA

Dr. Alexander Zucker
Retired
Oak Ridge National Laboratory
Oak Ridge, TN

Observers:

Dr. Everett Beckner
Vice President
Technical Operations & ES&H
Sandia-Lockheed Martin
Albuquerque, NM

Dr. Clayton Nichols
Chief Scientist
U. S. Department of Energy-Idaho Operations Office
Idaho Falls, ID

SCIENCE AND TECHNOLOGY INTEGRATION

P. M. Castle

Scope and Objectives

The INEEL has been designated as the Environmental Management Program laboratory. The Core Capabilities and Technical Enhancement Program (CCTEP) is a program that has been funded to maintain and enhance the INEEL's technical capabilities in order to address EM's waste management and restoration activities scientific and technical needs. The primary objective of the Science and Technology Integration (STI) Program is the creation and use of a system by which the DOE Environmental Management (EM) Program's unaddressed fundamental science needs can be effectively met by the CCTEP research and development activities.

FY 1998 Tasks

1. Design and document a process (roadmap) for the validation and maintenance of the technical content of the CCTEP portfolio of research activities

2. Integrate and analyze technology and science needs from a variety of sources

3. Perform a gap analysis using the data from Task 2 and the current CCTEP program content

4. Perform reviews of two research areas by external panels

5. Establish or maintain interfaces with the Focus Areas, EMI, and EMSP.

Technical Accomplishments

Background

The EM Office of Science and Technology (OST) has a variety of programs to assess and address technology development needs of the operational offices within EM. The technology and basic science needs are gathered by the Site Technology Coordination Groups (STCGs) and the EM Integration (EMI) activity. The focus areas (Tanks, Subsurface Contaminants, Mixed Waste, and D&D), the cross-cut programs (Robotics; Characterization, Sensors, and Monitoring Technology; Efficient Separations, Industry Programs, etc.), and the EM Science Program are the programs through which OST develops the technologies to address the identified needs.

One of the STI Program's functions is comparing the various technology development and basic science research activities sponsored by OST with the EM technology and science needs. The purpose of this analysis is to determine areas where the CCTEP can make contributions without overlapping activities sponsored by OST at other laboratories.

The EM technology development programs have been criticized during the last several years for not gathering input from sources external to DOE to aid in technology investment decisions. In order to avoid this criticism one of the STI program's objectives was the identification and recruitment of external advisory panels to provide technical input to each of the five technical areas in the CCTEP. The advisory panels were to be selected from outside the DOE Complex. The members of the panels for each of the five technical areas are to have backgrounds which match the spectrum of activities within each technical area.

An additional activity for the STI program was establishing and maintaining contact with the Focus Areas (Mixed Waste, Plutonium, Subsurface Contaminants) represented at the INEEL as well as working with the EM Integration (EMI) effort at the INEEL to be able to understand what science based needs might be indicated by the faulty links in the disposition maps.

FY 1998 Technical Accomplishments

This section will describe the activities and accomplishments of the STI program from February through September of 1998.

Needs Integration and Analysis

The process steps by which the CCTEP research and development portfolio was created and is maintained is shown in Figure 1. The current program was formulated using most of these elements. It is expected that the composition of the portfolio will be reexamined annually. Figure 1 shows the data sources to be used and activities that will occur. The need for an annual review of the program, in addition to maintaining good technical content, will be driven by budget fluctuations from year to year. Increases in budget will provide the opportunity to add activities to the portfolio or to enhance ongoing activities. In the case of declining budget it is necessary to have a process that provides the information needed to prioritize the individual activities within the program.

Two steps in the process in Figure 1, deficiency/needs integration and science issues identification, are at the core of the analysis of the program. Table 1 is the product of these two activities. The deficiency/needs integration activity involved gathering data from the sources shown in Figure 1. Using

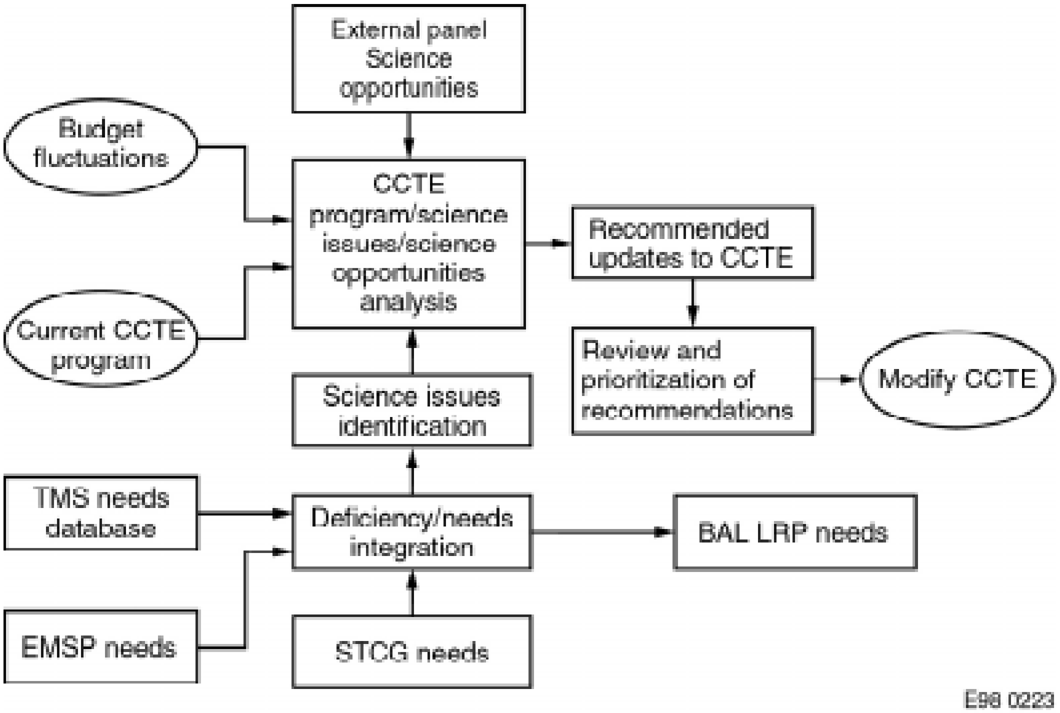

Figure 1. Process logic for the development and maintenance of the CCTEP.

Table 1. Relational groupings of Category 6 needs.

Sci/Tech		Biological Treatment	Need code
Both	6	Biological Treatment of Spent Solvents	AL-07-06-02-MW
Sci	6	Enzyme-Based Method for Destruction of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) and 2,4,6-Trinitrophenylmethylnitramine (Tetryl) Bulk High Explosive	AL-08-06-04-MW
Sci	6	Pretreatment of Explosives Contaminated Soil for Biological Remediation	ID-6.1.25
Tech	6	Biological Purification Of Gadolinium Nitrate From Heavy Water Moderator Ink	SR-6006
		In Situ Treatment	
Sci	6	In Situ treatment of mixed TRU tank wastes	ID-6.1.03
Tech	6	Treatment for MW Soils to Immobilize Radionuclides and RCRA Constituents for Disposal.	SR-1002
Tech	6	In Situ Grouting of Underground Tanks Formerly Used for the Storage of Radioactive Solvents	SR-3005
Sci	6	Treatment Technology For Groundwater Contaminated With Carbon Tetrachloride As A Dense Nonaqueous Phase Liquid In The Industrial Area	RF-ER02
		Tritium Management	
Tech	6	Treatment of Sorbed Tritiated Oil Waste	AL-08-02-09-SC
Sci	6	Treatment and Disposal of Tritiated Mixed Waste of High Specific Activity	Oakneed-3
Tech	6	Treatment and Control of Tritium-Contaminated Water	HY-18
Sci	6	Low-Level Radioactive Waste Landfill Cap Design, Tritium Treatment/Removal Technology, In Situ Vitrification, and Pressure Grouting	AL-07-02-03-SC-98
		Incinerator Secondary Waste Issues	
Tech	6	Technology to Reduce Mercury Emissions from the Consolidated Incineration Facility	SR-1018
Tech	6	Need to Reduce the Dioxin and Furan Emissions from the CIF	SR-1021
Tech	6	Volume Reduction and Stabilization of CIF Secondary Salt (NACL) Liquid Waste	SR-2047
Tech	6	Caustic Recovery and Recycle	SR-2048

the OST Technology Management System (TMS -http://ost.em.doe.gov/tms/Home/default.asp) database as the baseline information, needs were gathered from the sources shown. Next year's data integration activity emphasize the focus area and BAL LRP input more strongly than was the case for this year.

Once the integrated database was assembled, several types of analyses were carried out. A group of five scientists provided a consensus judgment for each need, identifying whether it was a science-based need or a more applied technology development need. It is easy to look at many of the needs assigned to the "technology development" category and see that basic science issues may underlie these needs.

Another analysis that was carried out was matching needs to the tasks and subtasks of the CCTEP. This assignment was carried out by the same group of scientists in a consensus mode. The numbers correspond to the top level research activities in the work breakdown structure for the CCTEP as follows:

1. Transport Aspects of Selective Mass Transport Agents
2. Chemistry of Environmental Surfaces
3. Materials Dynamics
4. Characterization for Optimization of Waste Processing and Treatment
5. Computational Physics, Chemistry, Geophysics, and Systems Analysis.

The needs associated with a 6 or 7 (which are not listed above) were deemed to fall outside the range of the CCTEP activities. Those needs found in category 6 are somewhat related in that they center on treatment or processing activities. Those needs assigned to category 7 appear to be things that will never fit within the current vision of the scope of the CCTEP.

Once the results of the categorization were compiled they were circulated to the research area leaders for each of the five CCTEP tasks for their review. Their comments on the validity of the assignments required little modification of the distribution of the needs over the research areas**.**

The category 6 needs have been collected in Table 1 and grouped by the type of need class to which they apparently belong. There are four groupings: Biological Treatment, In Situ Treatment, Tritium Management, and Incinerator Secondary Waste Issues. If there were to be any expansion of the scope of the CCTEP, the category 6 needs appear to be an area where there is not a strong overlap with the CCTEP technical activities.

The last column in Table 1 is the site priority ranking. These numbers were taken from the individual site 2006 Plans and were assigned by the sites. Care must be used in evaluating these priority numbers. Threes and twos may be just as important as ones in the sites' planning and may only differ in the period of time before which the need must be addressed. A one may be an imminent need (short-term) and a three a long-term need. From this point of view, the CCTEP's science may be more influential in addressing priority three needs. It is unlikely that much of CCTEP's science will be mature enough to be useful in addressing short term, high priority needs.

Advisory Panels. The decision was made to obtain technical input from advisory panels for two of the research areas—Transport Aspects of Selected Mass Transport Agents and Characterization Science for the Optimization of Waste Treatment and Processing. Two advisory panels were selected. The panel for the transport aspects of selected mass transport agents research area was chaired by Dr. Paula Hammond of MIT with the two other members being Dr. Benny Freeman of North Carolina State

University and Dr. Jerry Lin of the University of Cincinnati. The second panel for the research area characterization science for the optimization of waste treatment and processing was chaired by Dr. Mel Koch of the Center for Process Analytical Chemistry (CPAC), University of Washington. The other members of the panel were Drs. Lloyd Burgess and David Veltkamp of CPAC.

Presentations were made to the advisory panels in late August and early September. The agenda for these presentations included a background presentation concerning the mission and operations of the EM Program and its technology development activities. There was a subsequent overview of the CCTEP and its goals with respect to the EM program followed by technical presentations by the principal investigators. The members of the advisory panels provided helpful feedback at the time of the presentations. Each of the advisory panels has submitted a written report with their conclusions and recommendations. Overall the panels were impressed with the amount of work that has been accomplished in the short time since the program's inception. The information and recommendations from the reports will be utilized as input to the program evaluation and formulation process (as shown in Figure 1).

Interfaces with the Focus Areas, EMI, and EMSP. The focus areas, EMI, and the EMSP all have some level of understanding and data concerning technology development and technology requirements within the EM program. These program activities, funded by OST, have some overlapping data sources regarding EM technology needs and requirements. These overlapping data sources are not totally congruent. As a result there is a need to understand and integrate the information as discussed above. The focus areas and EMSP fund a variety of basic science research and technology development programs. The CCTEP needs to be aware of the research and technology development that is being funded elsewhere in order to assure the CCTEP is not duplicating other efforts.

There are interfaces with the Mixed Waste Focus Area (MWFA) and the Plutonium Focus Area (PFA) already in existence. The principal investigator for this program came from the MWFA technical staff and has attended PFA weekly staff meetings for 18 months. In addition he was part of the team that reconciled the original EMI disposition maps and the MWFA technical baseline and STCG needs for mixed waste. During the course of that exercise a good working relationship was established. The EMI has supplied the STI effort with the additional technology and science needs that were harvested during site visits to validate individual site disposition maps. EMI has indicated that it may call on the STI program to assist in the analysis of science issues associated with disposition maps in 1999. All of these interfaces and interactions will be continued in 1999.

In addition to the interfaces just discussed, the STI program began to work with the EMSP. The initial interaction was in support of the first site-specific EMSP workshop held at Savannah River in July. The purpose for the STI program's participation was to observe the process employed at the workshop with the intent of using it for a baseline model for workshops that the STI program might conduct. Since that time, the EMSP has showed interest in having STI personnel participate as full team members in EMSP activities.

Summary

The STI program has accomplished the tasks that it defined for 1998:

1. The design and documentation of a process (roadmap) for the validation and maintenance of the technical content of the CCTEP portfolio of research activities

2. The integration and analysis of technology and science needs from a variety of sources

3. The performance of a gap analysis using the data from Task 2 and the current CCTEP program content

4. The performance of reviews of two research areas by external panels

5. The establishment or maintenance of interfaces with the Focus Areas, EMI, and EMSP.

The information gathered in Tasks 2—5 will be used in the near future in the process that is described in Figure 1, the product of Task 1.

It is expected that in 1999 the amount of effort that will be necessary to be devoted to Tasks 2 and 3 activities will not need to be as great. It is not anticipated that the spectrum of needs will change dramatically over the next year. In addition, the structure for the database is already established and will be able to deal with additions or deletions as necessary. Additional external reviews will arranged to provide input for the remaining research areas. A greater emphasis will be placed on the communication of EM operations, needs and opportunities with the research area leaders and the PIs within the CCTEP.

The contributions of M. McIlwain and K. Daum in accomplishing the data integration task as well as the additional participation of R. Rogers, D. Maiers, and H. Heydt in the data and gap analysis is greatly appreciated.

RESEARCH LIAISON OFFICE

D. Maiers

Scope and Objectives

The Fractured Rock Science Team (FRST) Program was organized by DOE-ID to integrate interdisciplinary research activities conducted by onsite and extramural investigators funded through multiple sources. Currently the FRST consists of 14 research projects with basic research focusing on elucidating groundwater flow behavior, chemical interactions of pollutants with basalt surfaces, intrinsic processes that affect degradation of materials, microbial ecology, and field demonstrations of new technologies. Although each research project has its own specific goal, coordinating the research and active transfer of the results to cleanup programs will improve monitoring and cleanup processes in a fractured rock environment.

Specific organizations that will benefit by these coordination efforts are EM-40 (site cleanup programs), EM-50 (technology development programs, Environmental Management Science Program [EMSP]), ER-74 (Natural and Accelerated Bioremediation Research Program [NABIR], Subsurface Science Program [SSP]), and the Environmental Protection Agency. The products of this effort will support NABIR by serving as a model for its bioremediation test beds at national laboratories and provide a model for verifying and certifying remediation technologies. In addition, the integrated science program will leverage research dollars from EM-40, EM-50, and ER-70 activities to provide solutions to remediating and characterizing plumes in fractured rock.

The specific objective of this project is to establish a research liaison function to coordinate and assist with the conduct of environmental research at the INEEL. The functions of this liaison are to: 1) develop guidelines, or a decision tree, for how researchers will comply with site access, sample handling, and safety (environmental and personal) requirements while conducting work at the INEEL or with INEEL samples, 2) act as a single point of contact between researchers and INEEL ES&H, SMO, facilities, EM project personnel, and 3) to document the resource requirements (cost and time) for conducting research at the INEEL.

Technical Accomplishments

Several accomplishments were made during the short duration of this project. First, a research liaison office was established to be a single point of contact between researchers and the LMITCO ESHQ&A personnel as well as the LMITCO operations personnel. Second, a decision tree was developed for researchers to use as a guideline to determine what compliance requirements they would have to meet in order to conduct their specific research tasks. This decision tree enables researchers to understand the requirements, as well as the justification for specific requirements. Third, efforts were initiated to define the resource (time and cost) needs for meeting specific compliance requirements. This particular objective was not completed due primarily to the fact that many compliance activities were not evaluated because they were not needed by researchers during the short timeframe of this project. Fourth, a Generator Treatment Plan (GTP) was prepared for submittal to the state to achieve the approval to treat researcher generated waste (i.e., purge water resulting from well sampling) onsite. Another letter to the state was prepared requesting a “no longer contained in” determination for the treated groundwater. Together, when these two requests are approved, the FRST will have the ability to treat researcher-generated wastewater and dispose of it with minimal cost and complication. This issue has, in fact, been the primary reason that researchers’ tasks have been delayed during the 1998 sampling season.

Remediating groundwater below sites such as INEEL’s TAN presents an enormous technical challenge due to the great depths involved, the highly heterogeneous fractured rock environment, and the presence of an organic sludge/secondary source with high concentrations of TCE. In light of (1) the complexity of this remediation problem, (2) the commitment by DOE to meet remedial action clean up objectives within a 30 year operational period followed by 70 years of institutional control, (3) the importance of this water source, (4) the large number of researchers investigating pertinent aspects of this site, and 5) the complexity of compliance requirements for conducting research on a DOE-owned CERCLA site, the FRST was formed. This team subsequently identified technical research needs, as well as administrative hurdles, which need to be addressed in order to efficiently conduct research designed to ultimately improve remediation processes and technologies.

This specific task focused on defining, resolving, and minimizing administrative hurdles associated with conducting research on a DOE-owned CERCLA site. One product of this task was the development of a decision tree for researchers to use as a resource in defining the compliance requirements associated with their individual scopes of work and associated activities. Another product was the documentation necessary for the state to approve the treatment and disposal of sample well purge water resulting from the research activities. In addition to these products, a FRST Research Liaison Office was established in order to provide a focal point for communications between researchers and INEEL operations and compliance personnel. The establishment of this Office removed most of the confusion associated with an individual researcher having to make numerous contacts within the INEEL (a daunting task) in order to define schedule, compliance, and field support requirements. As a result, it is anticipated that research costs will be lower and schedules will be expedited.

The value of this task to the INEEL is recognized in numerous ways. It is resulting in the increased presence of outside researchers and collaborative opportunities. It is expected to be a model program for integrating other focused research programs. The INEEL, and specifically TAN, is likely to be designated as an environmental test bed for additional researchers and funding. And the cost of conducting environmental research is minimized while maximizing the results.