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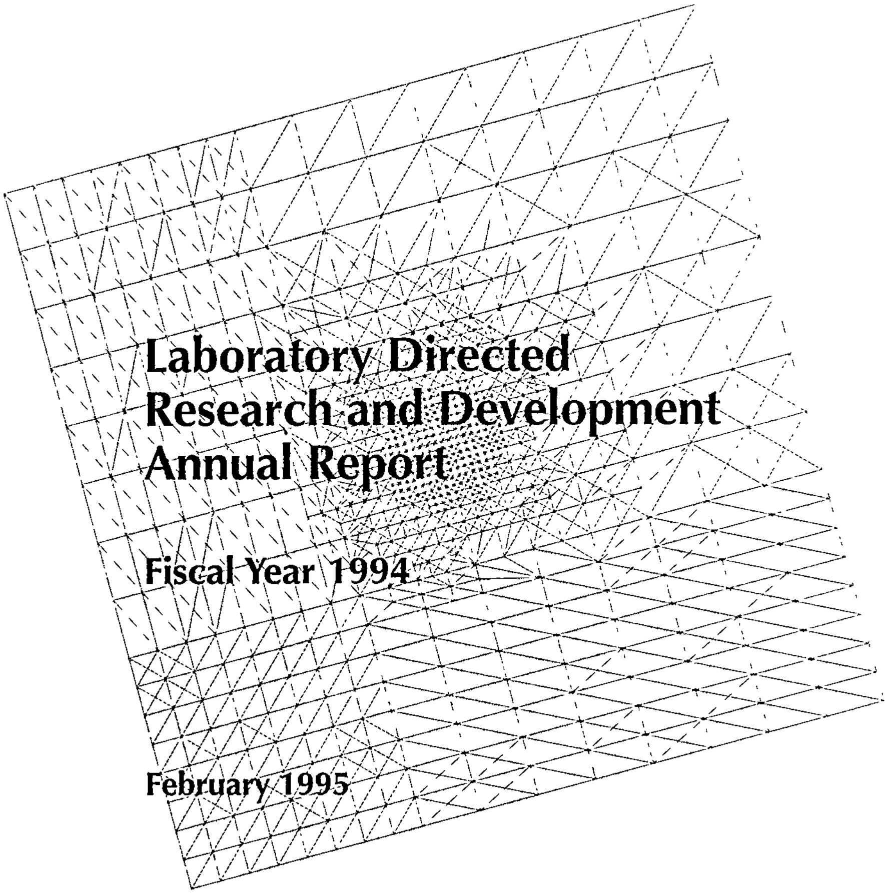

Laboratory Directed Research and Development Annual Report

Fiscal Year 1994

February 1995

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

Battelle

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
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Pacific Northwest Laboratory
Richland, Washington 99352

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Introduction

The Department of Energy Order DOE 5000.4A(a) establishes DOE's policy and guidelines regarding Laboratory Directed Research and Development (LDRD) at its multiprogram laboratories. As described in 5000.4A, LDRD is "research and development of a creative and innovative nature which is selected by the Laboratory Director or his or her designee, for the purpose of maintaining the scientific and technological vitality of the Laboratory and to respond to scientific and technological opportunities in conformance with the guidelines in this Order. LDRD includes activities previously defined as ER&D, as well as other discretionary research and development activities not provided for in a DOE program."

DOE Order 5000.4A requires that each laboratory submit an annual report on its LDRD activities to the cognizant Secretarial Officer through the appropriate Operations Office Manager. The report provided in this document represents Pacific Northwest Laboratory's (PNL's) LDRD report for FY 1994.

During FY 1994, 161 LDRD projects were selected for support through PNL's LDRD project selection process. Total funding allocated to these projects was $13.7 million. This amount represented 2.9% of PNL's operating budget, which is less than half of the 6% maximum allowed by DOE Order 5000.4A.

Consistent with the Mission Statement and Strategic Plan provided in PNL's Institutional Plan, the LDRD investments are focused on developing new and innovative approaches in research related to our "core competencies." Currently, PNL's core competencies have been identified as

- integrated environmental research
- process science and engineering
- energy systems development.

In this report, the individual summaries of LDRD projects (presented in Section 1.0) are organized according to these core competencies. The largest proportion of Laboratory-level LDRD funds is allocated to the core competency of integrated environmental research. Projects within the three core competency areas were approximately 91.4% of total LDRD project funding at PNL in FY 1994.

A significant proportion of PNL's LDRD funds are also allocated to projects within the various research centers that are proposed by individual researchers or small research teams. Funding allocated to each of these projects is typically $35K or less.

The projects described in this report represent PNL's investment in its future and are vital to maintaining the ability to develop creative solutions for the scientific and technical challenges faced by DOE and the nation. The report provides an overview of PNL's LDRD program, the management process used for the program, and project summaries for each LDRD project.

(a) U.S. Department of Energy Order DOE 5000.4A, Laboratory Directed Research and Development, 04-09-92.

Overview and Management Process

The strategic importance of Laboratory Directed Research and Development (LDRD), as well as the program benefits and the Laboratory's management process are discussed in this section.

Strategic Importance of Laboratory Directed Research and Development

The relevance and value of a Department of Energy (DOE) multiprogram laboratory lies in its ability to apply science and technology to national needs that fall within the missions of the DOE. The increasing complexity of these needs and the inadequacy of using conventional approaches demand that creativity and innovation underlie scientific and technological efforts so that new and novel solutions are discovered and applied. In addition, new ideas and opportunities frequently occur at a faster pace than can be anticipated or adopted in the federal budget process.

A national laboratory must establish and maintain an environment in which creativity and innovation is encouraged and supported if it is to fulfill its missions and remain viable in the long term. For these reasons, external reviews of the DOE multiprogram laboratories have consistently recommended that laboratory directors be given discretion to select research and development projects for support and to allocate a percentage of their operating budgets to provide this support.

The LDRD program, in the long term, allows the Pacific Northwest Laboratory (PNL) to assist DOE in fulfilling its missions and contributes to other priority needs of the nation. PNL's program supports creative endeavors in areas of strategic national importance that utilize the core competencies of the Laboratory. PNL seeks to continually replenish its inventory of ideas that have the potential to address major national needs. The principal goals of the LDRD program are to 1) encourage the advancement of basic science and fundamental research at the Laboratory, and 2) develop major new research and development approaches. Specific objectives are to

- foster an environment that encourages creativity and innovation
- fund new and novel ideas that have scientific/technical merit but that cannot be funded promptly through programmatic channels
- investigate new ideas/concepts to the proof-of-principle stage.

The LDRD program serves to enhance the morale and vitality of the Laboratory's scientific and technical staff and to recognize their importance to the future of the Laboratory. This program has a major impact on our staff by providing a specific source of funds that can be used to promptly pursue new ideas and concepts and enrich the Laboratory's core competencies.

Program Benefits

PNL's LDRD program has provided a number of benefits relative to the generic goals of fostering creativity and innovation within the Laboratory. The program has also provided specific benefits to PNL that have allowed it to assume a major role in the development of science and technology to address significant national needs, such as the environmental restoration of DOE sites and global climate change.

When PNL became an Energy Research laboratory in 1985, one of the major DOE directives was strengthening its fundamental research capabilities. A strengthened fundamental research component would establish a sound scientific basis for PNL's applied research and development programs that would provide a complete capability for the integrated management of scientific and technical programs of national importance.

LDRD has been the principal vehicle by which PNL has made substantial progress in improving its fundamental research base. The new capabilities developed at PNL in molecular science, high-performance computing, structural biology, and the environmental sciences have enhanced its ability to serve DOE missions. These new capabilities have changed and renewed the institutional vitality of PNL during a time when the Hanford Site was undergoing significant changes that appeared likely to undermine this vitality.

The national goal of restoring DOE sites, the total cost of which is now estimated to exceed $100 billion, will never be accomplished in a reliable and cost-effective manner without significant contributions from science and technology. These contributions will range from developing a fundamental understanding of the effects of contaminants on molecular structure and function, to developing innovative new technologies for processing wastes. Similarly, a rational and defensible approach to addressing global environmental change will not be developed until the nature of possible changes are more fully understood and the impacts of alternative mitigating strategies are analyzed.

The LDRD program has allowed PNL to initiate the process of bringing the capabilities of the national scientific and technical community to bear on these environmental problems. These efforts are still evolving and significant challenges remain. However, many of PNL's ideas and concepts related to these areas were originally developed with LDRD funds and are now receiving programmatic support from DOE. Examples include previous LDRD-supported work in the atmospheric sciences that is now being applied through PNL's participation in the Atmospheric Research Measurement (ARM) program, and studies in chemical dynamics that are now being supported by the Office of Basic Energy Sciences. It is believed that current LDRD projects in advanced processing and new energy technologies will produce similar scientific and technical benefits as national efforts in these areas more fully emerge.

PNL has traditionally made a portion of its LDRD funding available to small, interdisciplinary teams of researchers with new ideas or concepts that require only a small amount of funding (typically less than $35K) for initial testing. This practice is planned to be continued because of the significant scientific and technical benefits that have resulted. PNL's in situ vitrification (ISV) process, which is now receiving widespread testing and demonstration for use in remediating hazardous waste sites both within and outside the DOE complex was originally started through a $5K investment in testing a new idea brought forth by one of PNL's engineering groups.

In the current environment, the DOE laboratories are under pressure to increase their value to the nation. Important components of PNL's strategy in response to this environment are to 1) increase our productivity and 2) focus on addressing major national problems that can effectively utilize our core competencies. In this environment, the LDRD program becomes even more important as a key mechanism for achieving these goals and increasing PNL's value to the nation.

In summary, LDRD has enabled PNL to enhance its research vitality as a DOE multiprogram laboratory during a period of significant change. LDRD has facilitated PNL's ability to make significant contributions to addressing national problems, particularly in the environmental research area. It is essential that PNL and the other DOE laboratories retain the capability provided by LDRD if their full capacity to assist DOE and the nation is to be realized.

Laboratory Directed Research and Development Management Process at Pacific Northwest Laboratory

LDRD at PNL is funded through an overhead account applied to all technical labor hours charged to PNL's 1830 Contract accounts. Formal proposals in an authorized format are required for each LDRD project.

Decisions regarding funding levels for the LDRD account are made by the Laboratory Director. Primary responsibility for allocations to individual LDRD projects within these accounts rests with line and technical program managers, who assist the Senior Science Director in developing recommendations for the Director on these allocations.

All projects are reviewed for technical merit by line managers and/or scientific staff, and in some cases by external peer reviewers. Written guidance (including a formal LDRD Guide) pertaining to the criteria and guidelines for LDRD projects provided in DOE Order 5000.4A is widely distributed to PNL staff. Adherence to these criteria is further ensured through reviews by the LDRD Office. Individual projects are usually limited to $1M in total funding and $500K in a single fiscal year. The Director of Finance is responsible for financial oversight of the LDRD program. Accountability for individual LDRD projects rests with the principal investigators conducting the projects and their cognizant line manager.

The major sequential steps of PNL's LDRD process are illustrated in the figure. Additional details on these steps follow

- Based on the approval of PNL's LDRD Plan by DOE, initial funding allocations for LDRD accounts are approved by the Laboratory Director and disbursed by the Director of Finance.

- Line and program office managers solicit LDRD project proposals from research staff and select projects as candidates for funding. Each manager selecting an LDRD project must certify in writing that the project has been peer-reviewed and meets the requirements of DOE 5000.4A.

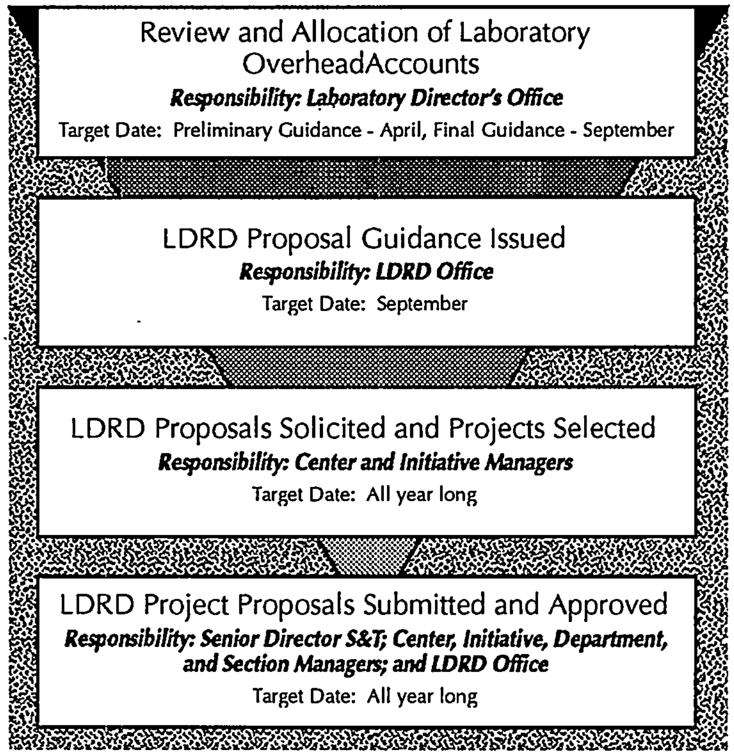
- All LDRD project proposals and the electronic files must be submitted to PNL's LDRD Office for review for compliance with DOE requirements after the principal investigator and the cognizant manager have signed them. All documentation required to meet National Environmental Policy Act (NEPA) and other environmental, safety, and health compliance requirements for the projects must also be submitted.

- The emphasis of the proposals is on the technical objectives and approaches that will be incorporated in the project.

- The Budget and Analysis Office has established four-digit alpha codes that are used to represent the work breakdown structure (WBS) code for each of the LDRD accounts. After a project receives final approval, a project-level work breakdown structure code is assigned by the LDRD Office for each LDRD project.

Primary responsibility for ensuring adequate technical review of LDRD projects rests with center and program office managers. In addition, regular reviews of selected activities are performed under the leadership of the Senior Science Director. A monthly LDRD seminar series also is used to review the technical status and highlights of selected projects. The various technical reviews constitute the most important means of ensuring that LDRD funds are used for their intended purpose.

Principal investigators and management are also required to develop input to meet all DOE LDRD reporting requirements. These requirements include the LDRD annual reports and the quantitative survey of LDRD project results. Selected principal investigators may also be asked to participate in annual DOE LDRD program reviews, which are organized by the LDRD Office. A group of 11 LDRD coordinators has been designated by PNL line managers to assist in managing and overseeing the LDRD program. The LDRD Office has primary responsibility for developing the annual LDRD Plan, with the concurrence of the PNL Senior Science Director and the Director of Finance.



1.0 Integrated Environmental Research

A Framework for Integrating Global Environmental Change Technologies Across Multiple Spatial and Temporal Scales

Lance W. Vail, Richard E. Rossi, Mark S. Wigmosta, and Ruby Leung (Earth and Environmental Sciences)

Project Description

One of the most perplexing tasks in global environmental change research involves integrating scientific technologies that represent processes at different temporal and spatial scales. For example, measurement of precipitation is accomplished at one scale (≤ 1 cm^2) while rainfall and runoff processes occur and are measured as streamflow at much larger scales (≈ 10 km^2). Furthermore, policy decisions (e.g., reservoir operations or irrigation scheduling) depend on the process models, but concern different temporal and spatial scales issues (≈ 500 km^2). Our goal was to begin to transcend the multiple scales inherent in the many scientific technologies concerned with global environmental change research in order to address policy issues by conducting research on an integrating framework.

Because integrating scale issues in global environmental change is fundamentally such a large topic, the work concentrated on the links among climatological, hydrological, and ecological research, as well as the statistical tools and physical models that link them. The focus of integration was water, specifically the precipitation (runoff, streamflow, evapotranspiration, vegetation processes) and linkages between them. Throughout the course of the project, however, other scales issues were also identified.

The reliability of global environmental change policy assessments depends on the ability of measurements, response models, process models, and policy models to interact with each other across the variety of temporal and spatial scales each represents. However, the inherent difficulties of breaching scales has limited the applicability of science-based process models to the needs of policy-driven agencies. Scaling difficulties have been further exacerbated by the problems of integrating data measured on different metrics and of varying degrees of quantity and quality (i.e., "soft" information). Furthermore, these measurements are also performed and processes are investigated by different disciplines and each tends to have its own language, methods, and scales of interest. Finally, global environmental change issues generally concern nonlinear processes, but there are few established statistical methods that deal with nonlinear averaging processes.

Technical Accomplishments

A series of four focused seminars were prepared and presented to a broad variety of technical experts. Topics of the seminars included: Scales Issues in Ecological Sciences, Scales Issues in Atmospheric Sciences, Scales Issues in Hydrological Sciences, and Advanced Methods for Addressing Scale Issues. These seminars provided enhanced understanding of scale issues across different scientific fields, improved communication among the various disciplines, and provided a demonstration of geostatistic's stochastic simulation technique for upscaling Hanford vegetation.

Promising techniques identified for addressing scales issues include the following:

- *Conditional Simulation.* Conditional (or stochastic) simulation is the application of Monte Carlo principles to correlated data. Typically, properties of interest are sampled at only a few locations, yet the behavior of a phenomenon is of interest over the whole sampling domain. For example, some measure of water quantity or quality may be known at specific locations, but concern is with the flow properties of environmental quality of the whole watershed. This sparse knowledge leads to a stochastic modeling approach. The idea is to construct numerical models of the watershed properties that honor (i.e., are conditional to) the available data. The technique builds multiple realizations which not only honor the data, they also honor the univariate and bivariate sample information. These multiple, equally probable images characterize and quantify the uncertainty in the spatial distribution of the reservoir properties. Decision analysis techniques may then be used to make risk-qualified decisions.

- *Minimum Relative Entropy.* Minimum relative entropy (MRE) is a method for deconvolving a pattern from large-scale data using Laplace's Principle of Insufficient Reason. In this approach, the "information entropy," a measure of pattern diversity, is minimized while preserving fine-scale measurements. As in the case of conditional simulation, minimum relative entropy allows the incorporation of "soft," as well as "hard" data. This approach has been used in fields ranging from pattern recognition to communications to irreversible thermodynamics.

- *Multiscale Orthogonal Decomposition.* Multiscale orthogonal decomposition techniques, such as wavelet transforms and multiscale interpolators, provide computationally efficient means of representing interpolated patterns exhibiting multiple scales of variability. They have the added advantage that they characterize the important scales of variability. This approach has been used in decomposition of spatial rainfall fields, pattern recognition, and signal processing.

- *Spatial Linear Averaging (SLA).* Once data fields have been generated on a fine grid, through data collection, disaggregation procedures, or via physically based process models, the simplest aggregation procedures provide the most straightforward solutions to the upscaling problem. Under spatial linear averaging, fine-scale data of additive quantities are simply averaged over a local neighborhood to obtain a larger scale rendition of the spatial pattern.

- *Nonlinear Averaging Filters.* In cases where the information to be upscaled relies in a nonlinear fashion on one or more interpolated fine-scale fields, these relations are incorporated in the form of a nonlinear filter. This approach is necessary when the information to be upscaled is difficult or impossible to disaggregate to fine scales, because of lack of data. In this way the nonlinear dependence of the large-scale variable upon small-scale fluctuations of the independent fields is captured through application of the nonlinear filter at small scales. This information is then upscaled via spatial linear averaging. For example, the inference of fine-scale soil moisture characteristics from remote sensing data involves such nonlinearities.

- *Non-Additive Aggregation.* In some situations, neither linear nor nonlinear approaches are adequate. For instance, hydraulic conductivities of surface soils on large scales are not linear averages of conductivities measured on smaller scales. In these cases, we use conditional simulation at fine resolution to estimate directly the statistical properties of the non-additive quantity on the larger scales.

Publications

R. E. Rossi. "The Geostat Low-Down on Up-Scaling," *Landscape Ecology* (in preparation).

L. W. Vail, R. E. Rossi, M. S. Wigmosta, and R. Leung. *Integrating Global Environmental Change Across Multiple Spatial and Temporal Scales*. Pacific Northwest Laboratory, Richland, Washington (in preparation).

A Multidisciplinary Investigation of Heterogeneous Atmospheric Processes

Rick D. Saylor and Richard C. Easter (Earth and Environmental Sciences)

Project Description

The goal of this project was to understand at a molecular level the uptake of gas-phase atmospheric pollutant species into aqueous droplets. This is being accomplished through a multidisciplinary effort involving macroscale atmospheric chemistry modeling, molecular-scale theoretical modeling, and surface second harmonic generation spectroscopy. The project was divided into three tasks: 1) the development and sensitivity testing of a multiphase atmospheric chemistry box model including detailed representations of gas-phase photochemistry, aqueous-phase chemistry, and interphase mass transfer; 2) the development of techniques for the molecular-scale modeling of processes occurring at gas-aqueous interfaces using molecular dynamics simulations and ab initio electronic structure calculations; and 3) the development of experimental techniques for measuring thermodynamic quantities and kinetic processes at gas/aqueous interfaces using surface second harmonic generation spectroscopy. The long-term result of this project will be an improved scientific and technological capability to study the importance of heterogeneous chemical processes in the context of global environmental change.

Technical Accomplishments

The following sections provide specific accomplishments in FY 1994 in each of the three project tasks.

Development, Testing, and Application of a Detailed, Mixed-Phase Atmospheric Chemistry Box Model

Progress in this task was slowed by difficulty in finding a suitable postdoctoral candidate to take on the development of the multiphase box model. We identified an individual (Dr. Yang Zhang) who has recently accepted a staff position in the Atmospheric Processes Group of the Earth and Environmental Sciences Center. Dr. Zhang will begin work on this project during FY 1995.

During FY 1994, literature searches were conducted to locate available information on the laboratory measurement of accommodation coefficients on liquid-phase surfaces. An informal report of the findings of that survey has been partially completed. This information will be useful to the progress of tasks 2 and 3. Additionally, literature reviews have been conducted to locate appropriate gas- and aqueous-phase chemical mechanisms to be used in the construction of the box model. Tentative selections of chemical mechanisms have been made. Literature reviews have also been conducted regarding other heterogeneous chemical processes that may be important in atmospheric chemistry and which can be included readily in the box model formulation.

Simulation of Molecular-Scale Processes at Gas-Liquid Interfaces

The first step of this task included modifications of the AMBER4 suite of molecular simulation programs to include capabilities that were required in the studies of gas-liquid interfaces planned for this project. After the code modifications were completed, an evaluation of interaction potentials for water was initiated. To date, simulations have used a pairwise additive interaction potential, the extended single point charge (SPC/E) model. In future work, we will compare these simulations with those using an interaction potential that includes many-body effects using a polarization model. The reliability of these models will be assessed by comparing experimental observables (such as surface tension and structural orientation) against the computed results. Preliminary calculations of the surface tension at room temperature with the SPC/E model yield a value of 67 dyne/cm that is in excellent agreement with the experimental value of 72 dyne/cm.

One interesting result of the initial simulations is the direct observation of the structure of the surface. The density of the water near the surface decreases, falling off smoothly to zero in the vacuum. This is not the result of the formation of a dense gas-like layer that becomes more diffuse further from the bulk liquid. Instead it results from the tendency of water molecules to form transient cavities in the liquid surface (see Figure 1). When averaged over time and distance, the cavities at the surface give a lowered density as compared to the bulk.

Measurement of Gas/Liquid Interactions at Water Surfaces Using Second Harmonic Generation Spectroscopy

During FY 1994, we reviewed the experimental possibilities for measuring properties of liquid water surfaces. In particular, we reviewed the literature of spectroscopic probes of liquid surfaces, and performed feasibility calculations in order to precisely define the experimental approach to be taken. Detailed experimental design has

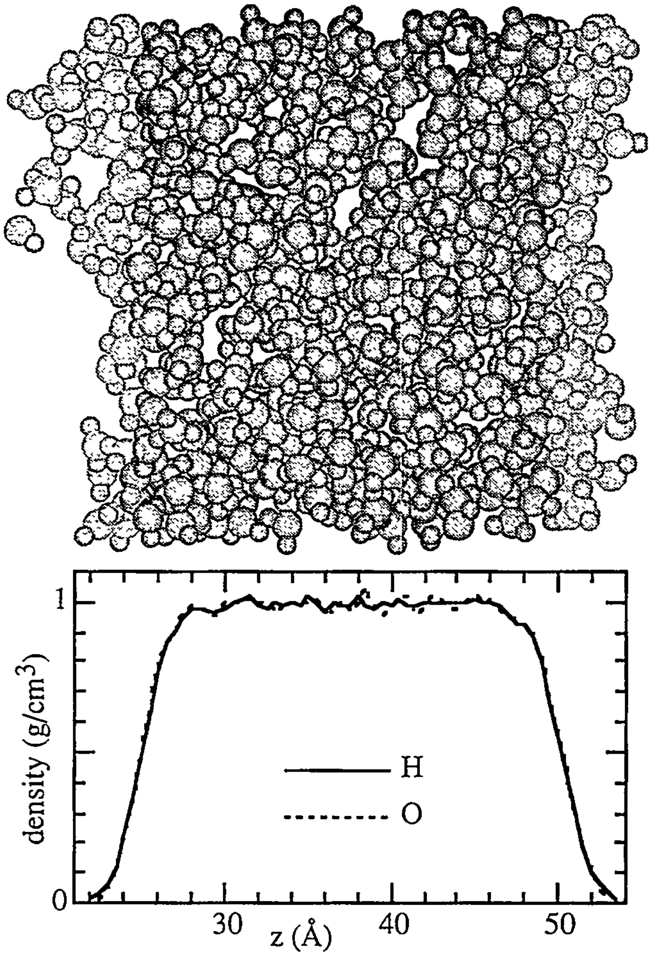


Figure 1. Snapshot of the gas-liquid interface of water and density profile as a function of distance perpendicular to the interface for a molecular dynamics simulation with 512 water molecules at a pressure of 1 atm and temperature of 300K. The lighter shaded water molecules are those that are in regions where the average density is lower than 0.5 g/cc.

now been compiled and setup of the experimental apparatus is under way. Completion of the setup phase and acquisition of initial data should take place early in FY 1995. A schematic of the apparatus is provided in Figure 2.

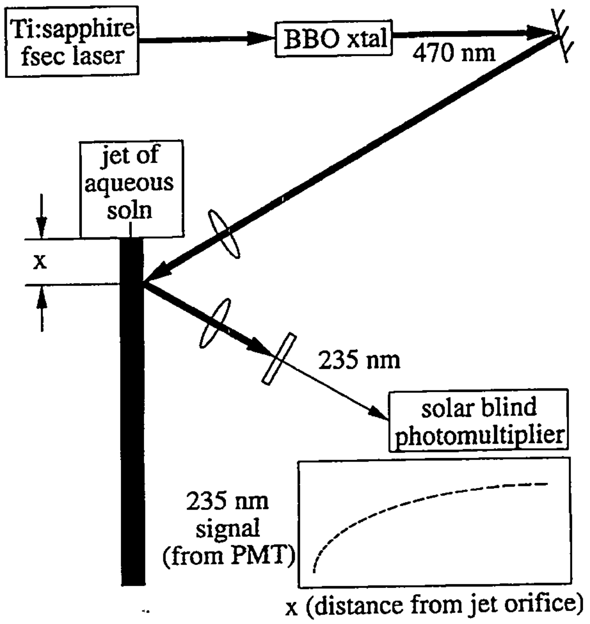


Figure 2. Schematic of apparatus for determination of thermochemistry and kinetics of gas-liquid surface processes via nonlinear laser spectroscopy.

Other Accomplishments

A postdoctoral fellow, Dr. Ramona Taylor, was hired and began working on the simulation of molecular-scale processes at gas-liquid interfaces in June.

A postdoctoral fellow, Dr. Robert Doolen, was hired and began work on the measurement of gas/liquid interactions at water surfaces using second harmonic generation spectroscopy during July.

Advanced Separations and Mass Spectrometry

Richard D. Smith (Chemical Sciences)

Project Description

The environmental cleanup of Department of Energy sites demands substantial advances in methodology and instrumentation for the analysis and characterization of environmental and biochemical materials. This project has focused on the development of new separations and tandem mass spectrometry and Fourier transform ion cyclotron resonance mass spectrometry methods for use in research into health effects and bioremediation, and a host of other areas benefiting from advanced and more sensitive characterization methods.

Technical Accomplishments

Important advances in biotechnology, structural biology, health effects research, and the development of a rational science-based approach to risk assessment would be derived from enhanced capabilities for the molecular level characterization of biological materials at ultra-trace levels and from very small volume samples. For example, methods to determine both the chemical identity and sequence-related sites of radiation and chemically induced DNA damage are needed. Environmentally relevant chemical and radiation exposure levels dictate that health-effects research relevant to environmental restoration address realistic exposure levels. Similarly, the ability to analyze the constituents of a single biological cell is presently extremely limited. The capability for structural characterization of many biochemical species (e.g., modified DNA, proteins, carbohydrates, etc.) is currently intractable for a variety of reasons, including their low absolute abundance and heterogeneity.

At Pacific Northwest Laboratory, unique capabilities for the mass spectrometric characterization of biomolecules with ultrahigh sensitivity and resolution now provide the basis for determining detailed structural information even for very large proteins and DNA fragments. Our aim has been to develop advanced methods based upon Fourier transform ion cyclotron resonance mass spectrometry (FTICR) and ancillary methods, and as appropriate its combination with fast high-resolution separation methods, that will directly address these needs in biochemical research. The combination of advanced high-resolution capillary electrophoresis and capillary liquid chromatography separations with FTICR provides the basis for characterizing mixtures of enormous complexity, or in more directed analyses, determination of specific components present at trace levels. The heart of these capabilities will be the world's highest field FTICR system based on a wide bore 12 tesla superconducting magnet.

In FTICR, ions are radially confined by an applied magnetic field (typically 1 to 7 tesla) and axially confined by a direct current trapping potential which is applied parallel to the magnetic field. The frequency of the cyclotron gyration of an ion is inversely proportional to its mass-to-charge ratio (m/z) and directly proportional to the strength of the applied magnetic field. The cyclotron radius of an ion, or an ensemble of ions, can be increased by applying a radio-frequency electric field that contains frequency components corresponding to the ions of interest. The nondestructive FTICR detection scheme can be used for ion remeasurement yielding improvements in sensitivity from multiple measurements of the same ion population. Tandem or extended multistage mass spectrometry studies can be performed on an ion population in which fragment ions of interest can be selected and retained in the cell, further dissociated, and detected again (i.e., remeasured), providing increased structural information with a significant improvement in overall sensitivity. As the cyclotron frequencies can be measured with high precision, the resulting mass spectra can yield ultra-high resolving power and mass measurement accuracy. This formidable combination of extended mass range, mass measurement accuracy, and resolving power is exclusive to FTICR mass spectrometry and provides a foundation for studies not readily tractable with conventional mass spectrometric instrumentation.

A unique attribute of FTICR which distinguishes it from all other forms of mass spectrometry is the ability to provide both ultrahigh resolving power and mass measurement precision without sacrificing sensitivity. The ability to distinguish species with very similar masses provides the basis for the direct identification of adducts, post-translational modifications, substitutions, and other variants. Additionally, mass resolution high enough to resolve the 1-Da spacing of peaks in the isotopic envelope allows unambiguous determination of charge (and thus mass) from detection of only a single charge state. Our electrospray ionization (ESI)-FTICR mass spectrometer has allowed the acquisition of extremely long lived transients (time domain signals) which yield spectra with mass resolving powers in excess of 10^6. A key attribute of the electrospray ionization process for large molecules is that their proportionally large charge states make dissociation reactions increasingly facile. Our laboratory first demonstrated that large multiply charged molecules could be efficiently dissociated by the use of high electric fields in the electrospray ionization interface, a process driven by the very large number of low energy collisions in this region.

The developments in FTICR now allow these processes to be effectively exploited for the first time.

The gentleness of the electrospray process coupled with nondestructive interface conditions permits the analysis of noncovalent complexes. For example, the reversible interaction of minor groove binders with nucleic acids has been explored. After annealing, the concentrations of 1:1 distamycin (Dm)/oligonucleotide duplex and oligonucleotide duplex will be equivalent if all of the distamycin binds to an oligonucleotide duplex. Ions representative of both the intact oligonucleotide duplex and the 1:1 distamycin/oligonucleotide duplex were observed in approximately equal intensities. The ability to ionize, trap, and detect such complexes creates new opportunities for the identification and study of selective binding with biomolecules.

It is generally recognized that the ability to couple online separation methods with mass spectrometry greatly increases its utility and flexibility in addressing complex samples. We have emphasized the combination of high-resolution separations by capillary electrophoresis (CE) with high-performance FTICR methodologies for application to biopolymers. Probably one of the greatest analytical challenges imaginable is the characterization of proteins from individual cells. The problem is immense due to the small cell volume, the low absolute quantities of proteins, the range of molecular weights, relative abundances, and the complexities due to the presence of salts and other constituents. The human erythrocyte (red blood cell) has been selected as an initial model system for single-cell analysis. Hemoglobin, its major constituent, is present at $\approx$ 450 amol/cell, making its detection challenging for mass spectrometric detection. By combining micro-manipulation techniques and in-capillary cell lysing techniques with the ultra-sensitive high resolution mass measurement capabilities of the CE-ESI-FTICR approach, we have recently acquired mass spectra of hemoglobin from as few as five intact human erythrocytes. Thus it appears feasible that combined CE-FTICR techniques will provide sequence information from cellular proteins directly from individual cells.

Publications

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J. A. Loo, P. Hu, and R. D. Smith. "Interaction of Angiotensin Peptides and Zinc Metal Ions Probed by Electrospray Ionization Mass Spectrometry." *J. Amer. Soc. Mass Spectrom.* (in press).

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Advances in Desktop Atmospheric Dispersion Modeling

Kenneth J. Allwine and Xindi Bian (Earth and Environmental Sciences)

Project Description

The objective of this work was to demonstrate that coarse-grained parallel computer technology can be applied to desktop atmospheric dispersion modeling by 1) preparing an easily upgradeable user interface and output package for the existing single-processor version of PGEMS, 2) determining performance characteristics (e.g., execution speed, accuracy) of the single-processor version of PGEMS, 3) identifying and purchasing a coarse-grained parallel computer, 4) installing PGEMS on the coarse-grained parallel computer, 5) demonstrating the potential for scientific improvement in PGEMS using parallel-processing by incorporating an advanced particle diffusion scheme into PGEMS, and 6) determining performance characteristics of the parallel-processing version of PGEMS and comparing these performance characteristics with the single-processor version of PGEMS.

Atmospheric dispersion models are used extensively for addressing atmospheric pathway issues including determining compliance with air quality regulations, responding to accidental releases of potentially harmful materials, planning siting of new facilities, performing required (National Environmental Policy Act [NEPA]) air quality assessments, providing input to other pathways analyses, and reconstructing historical exposures. The components of an atmospheric dispersion model are the user interface/input module, meteorological processing module (e.g., mean winds, turbulence statistics, temperatures, mixing heights), the topographic processing module (e.g., terrain heights, terrain roughness, surface cover), the transport module (includes diffusion, deposition, chemistry), and the post-processor/output module. Individual modules of the dispersion model may also be of use for special applications other than dispersion. For example, the meteorological processing module can be used to characterize the wind fields in a region. Consequently, the meteorological and topographic processing modules should be able to operate individually.

Over the past decade, staff at PNL have, and are developing, desktop dispersion models for several clients (e.g., Nuclear Regulatory Commission, Environmental Protection Agency, DOE, U.S. Forest Service, Pacific Gas and Electric). One model, PGEMS was initially developed several years ago for PG&E. It is based on the MELSAR model which was developed for EPA, and the MESOI model, which was developed for NRC. The PGEMS model is highly modular and the basic scientific components of the model are transportable to a wide range of computers. The user interface and input and output modules are, however, specific to a VAX computer with a Tektronix 4107 terminal, which, given the current advances in desktop computers, renders these interface modules sorely outdated.

Currently, revisions are being made to the meteorological processing module and transport module of PGEMS for installation on a DOS-based desktop computer as the emergency response model at PG&E's Diablo Canyon nuclear power plant. These current improvements, in addition to the general-use features of PGEMS, make it the preferred candidate model for implementation on a parallel processing computer proposed in this research.

Technical Accomplishments

This project began in FY 1993 during which time Mr. Xindi Bian initiated study of the PGEMS code, including a review of the source code and tests of the model over a range of input conditions. In FY 1994, an IBM 41T computer was networked with several IBM RISC 6000 model 590 computers capable of running the parallel virtual machine software for doing parallel-processing. A parallel-processing version of PGEMS was successfully developed and then tested on this network using the parallel virtual machine. We anticipate that we will be able to use the parallel virtual machine on the new symmetric multiprocessor computer, thus minimizing revisions to the parallel-processing version of PGEMS for installation and operation on the symmetric multiprocessor computer.

We also began developing a new diffusion module for PGEMS that bridges the gap between the simple puff diffusion scheme currently in PGEMS and the more physically realistic particle diffusion scheme. Particle diffusion schemes are too computationally intensive for applied models such as PGEMS operating on current-generation desktop computers. A paper describing the new diffusion scheme will be submitted for publication during FY 1995.

Aquifer Heterogeneity Identification

Charles R. Cole, Timothy D. Scheibe, and Christopher J. Murray (Earth and Environmental Sciences)

Project Description

A number of approaches to the modeling of heterogeneous aquifers were investigated, based on an existing model database. PNL currently has a highly detailed, finely resolved, three-dimensional, synthetic dataset representative of a geologically realistic aquifer system. This database was modeled after point bar sediments of the Wabash river system in the midwestern U.S.

Using this dataset as a comparative standard, we investigated a number of alternative models of the spatial structure of the natural heterogeneous system (geostatistical models). Several different models have been proposed in the literature for use in modeling the spatial distribution of hydrologic parameters (such as hydraulic conductivity) in heterogeneous systems. "Data" were drawn from a number of two-dimensional cross sections of the numerical aquifer and used to develop several stochastic models of the structure. Each model was then used to generate, in a Monte Carlo sense, several realizations of the model parameter distribution.

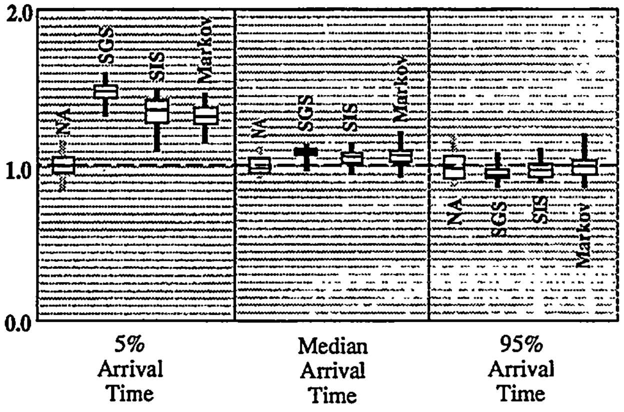
Each of the 12 sample cross sections from the numerical database (assumed ground truth) were used as input to a two-dimensional groundwater flow and transport model, to predict a number of measures of flow and transport behavior which would be of interest for practical environmental transport problems. Similarly, 50 realizations of each of the three geostatistical models considered were also subjected to flow and transport simulation. Therefore, the distributions of behaviors predicted using each of the geostatistical models could be directly compared, both to one another and to the distribution predicted using the numerical aquifer (assumed ground truth).

Technical Accomplishments

Three geostatistical simulation methods were studied: 1) Sequential Gaussian Simulation (SGSIM), 2) Sequential Indicator Simulation (SISIM), and 3) Markov Chain Simulation (Markov). Their predictions of flow and transport behavior were compared to those of the numerical aquifer (NA).

A sample realization from each of the three geostatistical methods and a sample cross section from the numerical aquifer were prepared. It was clear that, at least visually, the three simulation methods give quite different representations of the numerical aquifer's structure. Generally, all of the geostatistical methods diminish the continuity of individual beds to some degree, and all of the methods are unable to represent the multiple directions of continuity (different angles of bedding planes).

The figure shows box plots of the three predicted measures of flow and transport behavior. These indicate that for some behaviors, such as the early arrival time (5% arrival time), the geostatistical models introduce significant bias (model error). This model error is larger than the sampling error represented by the length of the error bars on the box plot, which represents sampling variability within the model due to parameter uncertainty. Note also that the model predictions are nonconservative in that they overpredict the early arrival, which would be of concern in a resource protection problem. This is a persistent problem with standard geostatistical models: Because of various assumptions required, these models tend to diminish the degree of structure in the actual aquifer. This problem is most significant for the SGSIM model, which is known to be the maximum entropy (least structured) model possible for given first and second spatial moments. For other behaviors, such as the median arrival time, the error introduced by the geostatistical model assumptions is much smaller, and there is little difference between the three models. Several measures other than the ones shown in the figure were also considered.



Box plots of selected measures of flow and transport behavior. NA refers to the Numerical Aquifer (ground truth); other plots represent three geostatistical simulation methods. All plots are normalized to the mean of the numerical aquifer simulation results. Box plots indicate the extrema of the distribution (vertical bar), the 25th and 75th percentiles of the distribution (ends of box), and the median (crossbar in box).

Geostatistical models (second-order bivariate spatial statistical representations) tend to provide biased model predictions of flow and transport behavior in natural aquifers, because they underrepresent the geometrically ordered, multiple-scale structure commonly observed in geologic systems.

The degree of model error is dependent on what measure of behavior is considered. Therefore, model selection and application should depend on the practical application of the model. Those applications which are sensitive to extreme behaviors, such as early or late arrival predictions, will be more significantly impacted by model assumptions than those which focus on mean behavior.

Additionally, collaborative ties with researchers at two other institutions (University of California, Davis, and University of Nevada, Reno) were developed. The collaborators were provided with the cross sections of the numerical aquifer and asked to provide realizations from models with which they have specific expertise. The Davis group is developing a Markov Chain model, more sophisticated than the one we applied here. The Reno group is applying a multi-fractual or wavelet model. Both groups' participation in this project was on a voluntary basis. Their results will be incorporated into the journal publication currently in production.

Publications

T. D. Scheibe and C. R. Cole. "Non-Gaussian particle tracking: Application to scaling of transport processes in heterogeneous porous media." *Water Resources Research* 30(7):2027-2039.

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Bonding and Structure of Organic Ligands at Oxide/Water Interfaces

Calvin C. Ainsworth (Earth and Environmental Sciences)
Donald M. Friedrich (Chemical Structure and Dynamics)

Project Description

The objective of this research was to examine the sorption chemistry of organic ligands at the solid-water interface by application of state-of-the-art optical spectroscopic methods. Research was performed to develop state-of-the-art sensitive spectroscopic methods using laser induced fluorescence (LIF) and high-sensitivity infrared spectrometry (FTIR) in novel ways that will allow spectroscopic interrogation of organic ligands at the solid-water interface at low sorbate surface coverage ($\leq 1\%$); and identification and characterization of the nature (bonding, structure, and dynamics) of interfacial organic species.

Technical Accomplishments

Interactions between organic ligands and minerals at the solid-water interface are integral to many processes occurring in soils and subsurface materials. These processes include contaminant transport, soil formation, and digenesis. Often, these interactions are characterized as surface complexation reactions and are assigned a structure based on inadequate data. In order to better understand and simulate important aqueous-mineral interfacial phenomena, it is crucial to obtain spectroscopic data concerning speciation, structures, and dynamics of organic ligands at the aqueous-mineral interface under controlled conditions that are still relevant to the natural environment.

Investigations were performed using salicylic and phthalic acids (mono- and diprotic acids, respectively) as probes and Al_2O_3 as the mineral interface. The two acids were chosen because they are both fluorophores and they are reported in the literature as model compounds for the study of organic ligand surface speciation (bonding, structure) as a function of important geochemical variables (pH, ionic strength, surface loading). Al_2O_3 was chosen because of its spectroscopically benign nature (infrared and ultraviolet transmittance, weak Raman interference). Most experiments are performed in constant temperature, dilute suspensions (1 g/L) of Al_2O_3, and low concentrations of the organic ligand (10^{-7} M).

Fluorescence spectra of sodium salicylate has been detected at levels of less than one salicylate ion per alumina particle. (At 10^{-7} M bulk concentration, 90% of the salicylate ions are adsorbed, corresponding to 0.7 molecules/particle in alumina suspension of 1 g/L rated at 100 m^2/g). This level of sensitivity was achieved with standard xenon lamp excitation through a single monochromator. In 1994, we achieved improved levels of sensitivity and signal/noise by means of polarized ultraviolet laser excitation. Use of laser induced fluorescence permit lower suspension loading which, in turn, will lead to reduced levels of stray-light scattering and improved measures of polarization anisotropy (discussed below). We estimate detection limits of salicylate with the current laser induced fluorescence apparatus to be less than 10^{-10} M.

A key advance from this year's research is the demonstration that fluorescence anisotropy measurements can be used directly to confirm and characterize the binding of organic acids to colloidal mineral surfaces in aqueous solution. The method of polarized emission is useful for determining the electronic structure and rotational dynamics of fluorophores. Polarized excitation light "photoselects" the subset of randomly oriented absorbers that have transition moments more or less parallel to the polarization vector of the excitation light. If the absorbers are prevented from rotational diffusion during the fluorescence lifetime, then the emission from that photoselected subset also will be polarized. Rotational diffusion can be inhibited in viscous solutions or by attaching the fluorophore to a slowly diffusing body in solution, such as a polymer chain or a colloidal particle. Emission anisotropy measurements have long been used to determine macromolecular dynamics such as protein folding.

Figure 1 summarizes the fluorescence results that led us to the conclusion that aqueous salicylate sorbs on colloidal alumina in at least two distinct chemical species. The fluorescence spectrum of salicylate anion peaks at 415 nm in pH 4.5 aqueous solution. Although not shown in Figure 1, when excited at 351 nm, the fluorescence spectrum of sorbed salicylate resembles that of aqueous salicylate (415 nm). However, this fluorescence is anisotropic with a polarization ratio ($N = I_v/I_h$) of approximately 2, suggesting that the species excited at 351 nm is anionic salicylate bound (i.e., not free to rotate on the nanosecond time-scale of the fluorescence emission) at the alumina surface (Figure 2). Excitation at a shorter wavelength reveals the existence of a second, bound species.

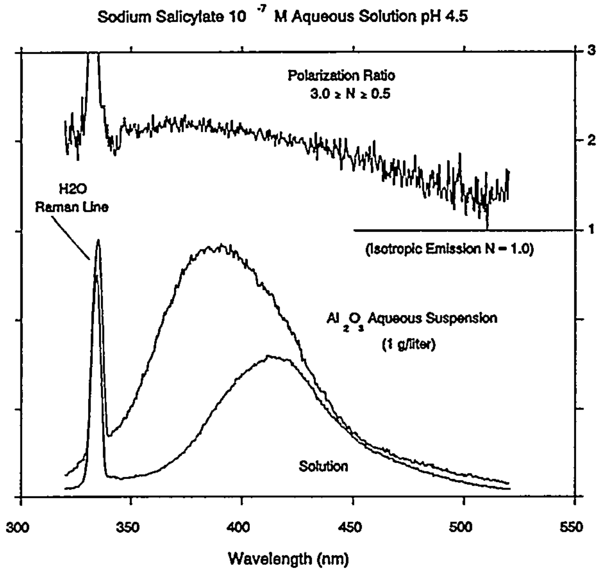

Figure 1. Fluorescence spectra and polarization ratio for sodium salicylate in pH 4.5 aqueous solutions excited at 300.1 nm. Bottom curve: 10^{-7} M solution fluorescence. Middle curve: 10^{-7} M salicylate sorbed (90%) to alumina colloidal particles (100 m^2/g) in pH 4.5 suspension (1 g/L). Top curve: spectral dispersion of fluorescence polarization ratio. For a sample of randomly oriented fluorophores excited by polarized light, the limits of the polarization ratio are $3.0 \geq N \geq 0.5$. The sharp peak in each curve is due to Raman scattering from water, which can be used as an internal intensity standard.

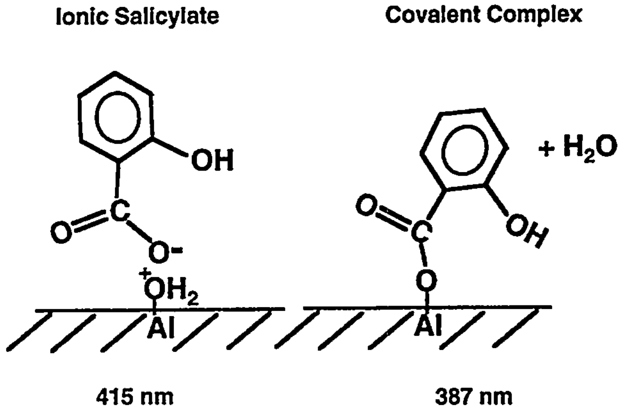

Figure 2. Proposed Structures of Sorbed Salicylate. The 415 nm fluorescence band is assigned to an ionic structure. The 387 nm fluorescence band is assigned to a covalent complex (aluminum ester of salicylic acid).

When excited at 300 nm, the fluorescence of sorbed salicylate exhibits a blue-shifted maximum (387 nm) and a diffuse shoulder (415 to 420 nm). Like the 415 nm fluorescence, the 387 nm band is also polarized, indicating another bound species. The blue shift is similar to the short wavelength emission of salicylate esters (such as methyl salicylate) in which intramolecular hydrogen-bonding is prevented by protic solvents. Therefore, we tentatively assign the 387 nm fluorescence to the covalent salicylate-alumina complex (Figure 2).

If the adsorption of salicylate to alumina is performed at pH 6 and increasing background electrolyte ionic strength, the intensity of the local maximum decreases as ionic strength increases. This decrease is not observed at pH 4.5. The effect of ionic strength on the intensity of the local maximum is coincident with that observed for the surface concentration of salicylate and pressure-jump relaxation events. These data suggest that there are at least two distinct surface complexes on the alumina surface: the response of the 387 nm maximum and the 415 nm maximum to ionic strength and pH changes correlates to an inner-sphere and outer-sphere surface complex, respectively. Recent acquisition of a cryostat for fluorimetry will enable improved spectral resolution of fluorescence bands by excitation of the samples at low temperature. Identification and characterization of inner-sphere and outer-sphere salicylate species are being accomplished by means of fluorescence anisotropy, quantum yield, and lifetime measurement.

Publications

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Catalytic Chemistry of Metal-Oxides

Charles H.F. Peden (Materials and Interfaces)

Project Description

This project studied the chemistry and catalytic properties of metal-oxide materials. While the surface chemical properties of metal-oxides affect an enormous number of environmental and energy problems and potential technological solutions, a general absence of detailed studies on well-characterized systems has prevented progress in developing a fundamental understanding in this area. The results of this research can potentially be used to understand an important class of novel, superacidic oxide catalysts being developed at PNL in order to improve these materials.

Technical Accomplishments

Transition metal oxides have found numerous applications as heterogeneous catalysts for other industrially important processes, such as the selective oxidation, isomerization, and metathesis of hydrocarbons, and the selective catalytic reduction (SCR) of NOx. In spite of their importance, oxide catalytic materials and processes have received much less attention from a fundamental science point of view than have catalysis by metals. For this reason, we have initiated a fundamental study of the catalytic properties of oxide materials. Funding was used for the following tasks:

- surface analytical and high-pressure kinetics measurements on high-surface area catalysts and on model oxide substrates
- complementary spectroscopic measurements on both high-surface area materials and more structurally well-defined surfaces.

In the few months that we have conducted work on this project, we made considerable progress on the completion of a unique high-pressure catalytic reactor/ultrahigh vacuum (UHV) surface science apparatus capable of conducting kinetic and mechanistic studies of catalytic reactions on well-defined single-crystal oxide surfaces. Interim experiments were performed in collaboration with Dr. David Belton of General Motors Research Laboratories to develop an understanding of NO reduction over supported metal catalysts to contrast with the behavior of oxide catalysts.

In these studies, we examined the effect of surface structure on the NO-CO activity and selectivity by comparing the reactivity of Rh(110) and Rh(111) single-crystal catalysts. These studies are motivated by many reports demonstrating that the selectivity for the two possible nitrogen containing products from NO reduction, N_2O and N_2, are dependent on Rh loading in supported catalysts. We have studied the effects of temperature, NO conversion, and NO-CO ratio on the activity and selectivity of the NO-CO reaction at high (1 torr $<$ P $<$ 100 torr) pressures over the two Rh single-crystal surfaces. We have used the results to rationalize the behavior of realistic supported Rh catalysts for this important automobile exhaust catalytic reaction. While we find relatively small differences in the NO-CO activity over Rh(110) and Rh(111), we find large differences between these surfaces with regard to their selectivities for the two competitive nitrogen-containing products, N_2O versus N_2. The more open Rh(110) surface tends to make significantly less N_2O than Rh(111) under virtually all conditions that we probed with these experiments. An example of these results is illustrated in Figure 1 showing the N_2O selectivity, $_{S}N_2O$ J (mol N_2O1/[mol N_2O + mol N_2]), as a function of NO partial pressure at a constant CO pressure of 8 torr on the two single-crystal surfaces we studied. These results can be understood in terms of the relative surface coverages of adsorbed NO and N-atoms on the two surfaces under steady-state reaction conditions in that higher N coverages on the (110) surface favor N-atom recombination (N_2 formation) more than the

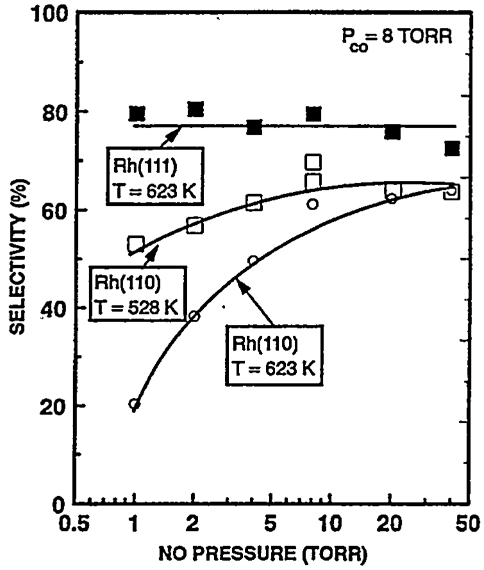

Figure 1. Selectivity of Rh(111) (T=623K) and RH(110) (T=528K and T=623K) surfaces as a function of no pressure.

NO+N reaction (N_2O formation) on Rh(110) relative to Rh(111). These conclusions can be tested by making an indirect assessment of the state of the reactive surface with x-ray photoelectron spectroscopy (XPS). This technique can clearly distinguish between adsorbed nitrogen present as either molecular NO or as N-atoms formed by NO dissociation during reaction. For Rh(111), the spectrum shows only a single N(1 s) feature with a binding energy near 400.3 eV due to adsorbed NO. In contrast, the NO N(1 s) feature on Rh(110), while present, is significantly smaller than another N(1 s) feature at lower binding energy, 397.6 eV, due to adsorbed N-atoms.

We also initiated experiments on the catalytic reduction of carbon tetrachloride over oxide-supported catalysts. This work resulted from discussions between Paul Ellis and staff scientists at Union Carbide that suggested that alumina-supported silver catalysts might be particularly active for the cleavage of carbon-halogen bonds under reducing (H_2) atmospheres. As a test case, the following reaction was studied:

$$CCl_4 + 2H_2 \rightarrow CH_4 + 4HCl \qquad (1)$$

A simple plug-flow reactor design was used with the reaction products passing through a gas cell mounted in an infrared spectrometer for detection and quantification. The results of a typical run are shown in Figure 2 for reaction temperatures above 450K. The results clearly demonstrate the ability of the supported silver catalyst to activate carbon-halogen bonds, and that the catalyst was also capable of subsequently hydrogenating the (presently uncharacterized) carbon deposits.

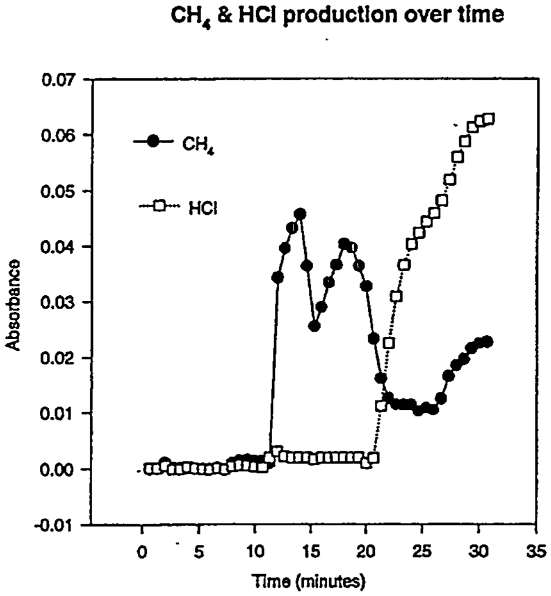

Figure 2. Infrared absorbance signals as a function of time for CH_4 and HCl formed by the catalytic reduction of CCl_4.

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Characterization of Structure and Dynamics of Surface Adsorbates and Their Surfaces

Paul D. Ellis (Macromolecular Structure and Dynamics)

Project Description

The solid-state nuclear magnetic resonance spectroscopy of four surface systems was carried out. The first project involved the continued characterization of ethylene adsorbed to supported silver catalysts. The main objectives of this research were to determine the structure (CH and CC bond distances) and dynamics of the adsorbate ethylene, characterization of the consequences of adding various promoters to the surface and the effects these have on the structure and dynamics (e.g., Cs^+ ions), and characterization of the work function for the silver surface and how it changes in the presence of differing supports and added promoters.

The second task deals with the characterization of surface molybdenum sites on hydrodesulfurization (HDS) catalysts. This project will pursue questions relating to the utility of the combining cross-polarization and dynamic angle spinning (DAS) experiments as a means for determining the various molybdenum species present on the surface of the hydrodesulfurization catalyst.

The third task will address the specific details associated with the characterization of quadrupolar nuclides via a general line shape procedure. The questions to be addressed include species identification, their number and relative amounts, the separation of quadrupole and shielding effects, the accuracy of the determination of the relevant nuclear magnetic resonance parameters, and a characterization of their dynamics. The final project to be addressed is the characterization of the dynamics of proton motion of the surface of aluminas.

Technical Accomplishments

The first two objectives of this project rely on the existence of a robust line shape program for the disentanglement of multiple tensors from a nuclear magnetic resonance line shape. The Hamiltonian describing the quadrupolar and chemical shift interactions has been presented through an irreducible tensor derivation. Some potential ambiguities concerning the sign of the asymmetry parameters, in this nomenclature, have been identified and clarified. A more robust algorithm for handling the boundary conditions imposed by the constraints on asymmetry parameters has been described and implemented in a nonlinear least squares minimization procedure. In addition, a detailed account has been given on a more efficient method for computing the nuclear magnetic resonance line shape, and protocols for the extraction of nuclear magnetic resonance parameters from solid-state line shapes have been introduced.

A novel aspect of the work was the extraction of tensor information directly from the experimental spectra via a SIMPLEX, and the MINPACK implementation of the Levenberg-Marquardt algorithm used to obtain more reliable experimental observables. Further, a complete error analysis is also provided as part of the line shape analysis. As in all of these approaches, the procedures are computationally involved, and the potential for the experimentalist to be "trapped" in a false minima is a concern. In this work, we detail a more efficient method for computing the nuclear magnetic resonance line shape and introduce protocols for the extraction of the parameters from solid-state line shapes.

Figure 1 summarizes our present status with respect to the characterization of the carbon-carbon distance in adsorbed ethylene as a function of added promotor ion, Cs^+. The data were collected on the 400 MHz spectrometer here at PNL at 67K. The left portion of the figure has 0% added Cs^+. Note the change in the line shape with 20% added Cs^+(right side). The bond distance extracted from the line shapes is 1.34Å (0%) and 1.37Å (20%). While the dipolar tensor has rotated 20 degrees relative to the shielding tensor, the quality of the fit is not what is expected as yet. The reason for this is that we have not included the information from the monolabeled ethylene. We expect to perform these experiments in the near future. What these experiments clearly show is that the promoter affects the electron distribution in the ethylene; presumably, by donating electrons to the anti-bonding orbitals. The main question to be addressed is how, i.e., either via a direct process—such as a complex or indirectly through the conduction electrons of the silver.

The SEDOR experiment will distinguish between these two possibilities. This experiment will allow the determination of the distance between the Cs^+ atom and the ^1H's on the ethylene. The sensitivity of the experiment to distance is depicted in Figure 2. Clearly the method is sensitive to distances in the range 2 Å to 6 Å. The experiment requires that the sample be at liquid nitrogen temperatures to remove most of the motion in order to prevent dipolar averaging.

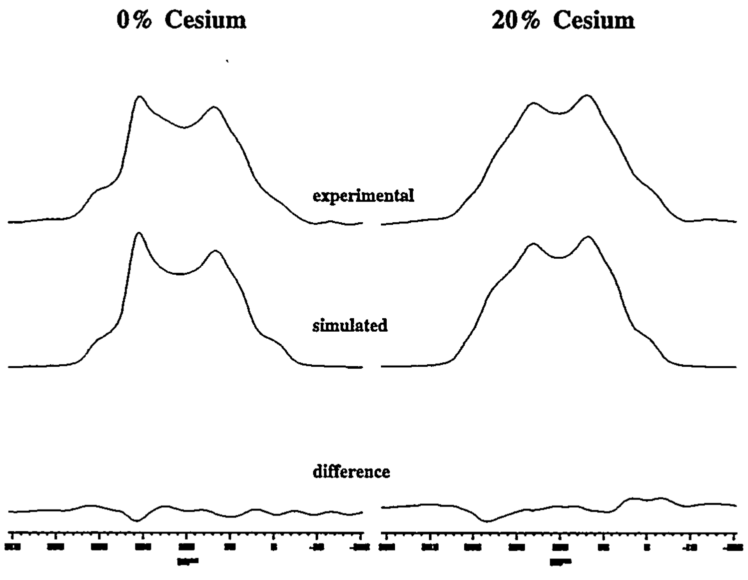

Figure 1. Characterization of Carbon-Carbon Distance in Absorbed Ethylene

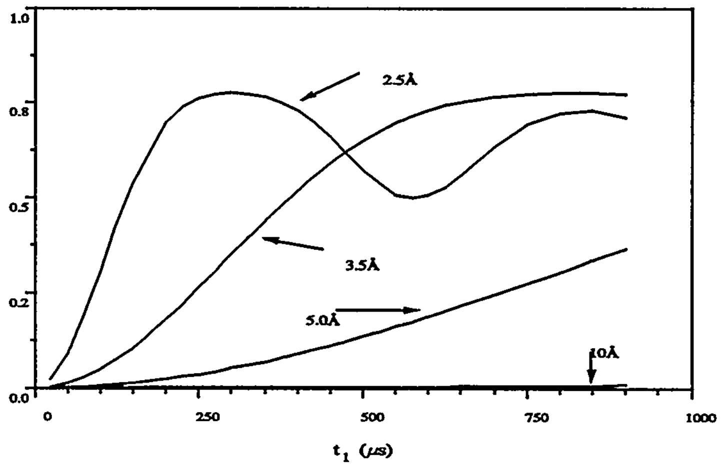

Figure 2. Sensitivity of Experiment to Distance

Publication

J. M. Koons, E. Hughes, H. M. Cho, and P. D. Ellis. "Extracting Multitensor Solid-State NMR Parameters From Line Shapes." Some Comments and Protocols, *J. Magn. Reson.* (in press).

Chemical Dosimetry

Gamal Akabani (Health Protection)

Project Description

The objective of this study was to determine the levels of detection of carbon monoxide in porphyrins molecules. The development of optically stimulated luminescence capabilities have provided us a vast array of optical tools, such as sensitive light detection devices, a wide range of lasers and light sources, a spectrophotometer, and an optical multichannel analyzer. The same tools that provided the analytical backbone of the optically stimulated luminescence research program were ideally suited to application in the development of chemical dosimeters.

Biological risk from a chemical pathogen results from complex biochemical reactions leading to the disruption of one or more biological processes. In order to effectively monitor for environmental chemical pathogens, it was necessary to assess the feasibility of developing a chemical dosimeter with certain characteristics. The ideal chemical dosimeter must possess the following qualities:

- Specificity - Any detection technique must be highly specific. Risk is generally linked to the alteration or disruption of complex biochemical processes. Thus, the ideal chemical dosimeter would need to mimic the actual chemical process leading to biological risk.

- Sensitivity - Any chemical dosimeter must be sensitive enough to measure exposure levels below or near the maximum permissible working concentrations.

- Practicality - The ideal dosimeter must evolve in a similar fashion to the current radiation dosimeter. The dosimeter must be cost-effective, small enough to wear at work, easily analyzed, and compatible with a wide range of operating environments.

Technical Accomplishments

The following tasks were carried out during this project.

Development of a Carbon Monoxide Chemical Dosimeter

The heme macromolecule contains a porphyrin ring system that is capable of reversible chemical bonding of oxygen and carbon dioxide. Stearic constraints limit the bond strength of the porphyrin ring system to oxygen and carbon dioxide. Carbon monoxide has no stearic hinderance and is, therefore, capable of very tight binding to the porphyrin molecule. In fact the carbon monoxide molecule occupies a permanent site on the porphyrin molecule and renders the site incapable of performing its biochemical function of transporting oxygen and carbon dioxide through the blood stream.

Bonding of carbon monoxide to the porphyrin ring system alters the optical characteristics of the molecule that can be measured using sensitive spectroscopic techniques. It may also be possible to measure laser fluorescence of the altered porphyrin molecule. This task involved obtaining porphyrin molecules and producing a solution that can be measured both before and after carbon monoxide exposure. Analytical measurements of optical absorbance and laser fluorescence measurements were performed. These measurements provided the basis for engineering a practical chemical dosimeter to measure carbon monoxide.

Initial experiments with blood from dogs were carried out using carbon monoxide introduced in minor quantities into the blood system; discouraging results were obtained by the spectrometer that did not register any changes in the mass absorption spectrum of blood itself for the different concentrations of carbon monoxide used. This experiment was carried out several times to eliminate all possible systematic errors and changes in measurement methods. Other toxic gases were used with the same negative result. Water was used to dilute the blood before reading in order to be able to read some small changes; however, these measurements were inconclusive as many experiments were not conclusive in their results.

Identification of Other Chemical Hazards

This task identified other chemical hazards and developed a methodology similar to the carbon monoxide chemical dosimeter model. The biochemical processes leading to the pathenogenic nature of other chemicals was investigated and a few promising systems were proposed for further study consistent with the dosimetric philosophy of the carbon monoxide chemical dosimetry system.

Chemical Sensors

Jay W. Grate (Materials and Interfaces)

Project Description

The objective of this project was to develop a new capability to examine, at the microscopic level, the interaction between environmental pollutants and chemically selective sensor materials, the kinetics and thermodynamics of processes occurring at these interfaces, and to develop the understanding required for rational chemical and physical modification of materials for integration into chemical sensor devices. Additional work was directed at the development of advanced sensor calibration techniques that will ultimately enhance the sensitivity and selectivity of sensors and arrays of sensors.

Technical Accomplishments

New Suspended Gate Field Effect Transistor (SGFET) sensors with temperature controlled gates have been designed and fabricated. In this second generation of SGFETs, the gate electrode and the resistive heater are electrically insulated which enhances the sensor performance. The temperature profiles of both the electrically heated gate and the substrate in the gate vicinity are critical sensor characteristics. These have been investigated with an infrared microscope on a micrometer scale. The temperature measurements performed on the dual gate SGFETs indicate that crosstalk between the individual sensing elements located on one chip is minimal. These results demonstrate the suitability of the SGFET design for the fabrication of a gas microsensor array with individual sensing elements operating at different temperatures.

A number of chemically sensitive layers for the SGFET sensor application have been developed. Electrochemically prepared poly(oxyphenylene), palladium, polyaniline (PANi), PANi/Pd, and PANi/Fe composite thin films have been investigated. Responses of these layers to hydrogen, ammonia, and nitrous oxide diluted both in nitrogen and air have been analyzed using a Kelvin Probe, which is a macroscopic equivalent of the SGFET. The layers showed logarithmic response to hydrogen in air with dynamic range spanning more than 3 decades. The influence of the operating temperature and the presence of water vapor has been studied. The results indicate that the SGFET sensor with the newly developed chemically sensitive layers has great potential for monitoring particular gas concentrations with severe fluctuations of concentration even in the presence of other interfering species.

The state of the art regarding bulk acoustic wave sensors (generally called quartz crystal microbalances, QCM) has been advanced by research directed toward extending quartz crystal microbalance applicability to liquid phase sensing. The dual quartz crystal microbalances (DQCM) show excellent stability in aqueous environments, even as temperature, viscosity, and conductivity of the liquid are varied. Immunity to these variables is important for environmental sensing applications. Using chemically sensitive polymers identified by the polymer portion of this LDRD, DQCM probes to date have demonstrated 10 ppm sensitivity to trichloroethylene in nitrogen gas and 1 ppm sensitivity to carbon tetrachloride dissolved in water.

Flow injection analysis techniques have been developed for the analysis of hexavalent chromium in soils and groundwater. Initial work focused on automating an Environmental Protection Agency approved reagent chemistry for selective colorimetric detection of Cr(VI) in water. This new sequential injection procedure requires only 500 microliters of sample, of which 50 microliters are analyzed, and generates a total secondary waste volume of 1.5 milliliters for each analysis. The analysis can detect Cr(VI) concentrations from 10 ppb to 5 ppm in water, and each sample requires less than 2 minutes per analysis. The method has been extended by incorporating an automated soil extraction procedure to leach Cr(VI) from soil samples and analyze the extracts by the same method. A new analytical procedure for chloride analysis using reflectance detection was developed. Spin-off work from the flow injection analysis capability set up under the LDRD funding has included using sequential injection techniques to automate radiochemical analysis, and using continuous microscale flow methods to simulate waste processing steps.

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J. W. Grate. 1993. "Sensing Glass Transitions in Thin Polymer Films on Acoustic Wave Microsensors." Presented at the North Coast Thermal Analysis Society Meeting, Cleveland, Ohio (invited).

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Collaborative Environment Prototype for Molecular Science

Richard T. Kouzes (Computing and Information Sciences)

Project Description

The objective of this project was to develop a prototype collaboratory environment for molecular science research. A collaboratory is a "laboratory without walls" that spans multiple geographical areas with collaborators interacting via electronic means. These collaborations may involve theoretical, computational, or experimental research. The collaboratory concept provides an open meta-laboratory which enables close ties between scientists in a given research area, promotes collaborations involving scientists in diverse areas, accelerates the development and dissemination of basic knowledge, and minimizes the time-lag between discovery and application. Creating a collaboratory entails integrating computing tools to produce an environment where multiple, geographically separated researchers can collaborate on experimental and analysis tasks.

A central component of a collaboratory is a scientific computing environment that provides for the integration, synthesis, and management of information from all sources (instrumentation, theory, computation, literature, etc.), and the resources for accessing and manipulating that information in a consistent, efficient manner.

Technical Accomplishments

This project started in June 1994. We have developed a prototype Collaborative Software Environment (CSE) integrating collaborative tools.

A preliminary evaluation of the needs of researchers for electronic collaborative capabilities was performed. Software tools for collaborative work include network-based concurrent window display, video conferencing, shared whiteboards, hypertext information access, and collaborative scientific notebooks. An initial tools set has been assembled and integrated into a collaborative environment for nuclear magnetic resonance. Specific tools have been selected and are being integrated into the prototype.

- A PNL developed executive launches the tools on the desktop, keeps track of which collaborators are connected and which tools they are using, and provides a shared chat box for message exchange.

- Audio and video teleconferencing and shared whiteboards are other required tools, and are available in the Lawrence Berkeley Laboratory MBONE software, as well as commercial applications. Teleconferencing provides a real-time, non-permanent interaction mechanism.

- The ability for multiple collaborators to simultaneously observe (and potentially interact) with an analysis program or an instrument console (televiewing) is one tool. We are evaluating xmx, which is a televiewer for UNIX platforms. We are also developing a cross-platform televiewer since we have not located a public tool which satisfies this need.

- A collaborative scientific notebook provides a shared, integrated, multimedia, cross-platform, permanent data storage mechanism for scientific information. The Virtual Notebook System (VNS) from The Forefront Group is a commercial tool of this nature, available for Macintosh, MS Windows, and UNIX platforms. It allows users to create text, images, and other "objects," arranged on "pages" in "notebooks" that can be viewed and changed by multiple simultaneous users. The notebook allows real-time interaction between collaborators and provides a permanent record of the interaction.

- NCSA Mosaic provides a World Wide Web hypertext document browser, as well as a platform for integrating information access which is required for the collaborative environment. The web provides text, graphics, audio, and video in a relatively noninteractive, but permanent, form.

Collaboratory developments efforts in the realm of molecular beam reaction dynamics (MBRD) have been directed at supporting collaboration between researchers in molecular beam science. These efforts have resulted in the first deployment of a number of the tools described above to support general collaborative activities in this field and also the development of a number of in-house, custom software tools to meet specific needs of the scientists. Experimentalists and theorists in three different groups at the University of Utah and the PNL have been connected over the Internet and can now make use of the Virtual Notebook System to exchange and store text, graphics, and other information on UNIX, PC, and Macintosh computer platforms. The theorists on the project at PNL can store images of molecular structures and diagrams of vibrational motions they have calculated to be used by the experimentalists at the University of Utah in their modeling efforts of collisionally induced dissociation reactions. Our own development efforts have included the creation of reusable extensible software tools for facilitating the development of distributed programs.

Modules for handling network communication and the interactive display of graphical scientific data have been built and may be essentially "dropped in" to future applications. Using these tools, a program has been developed for the simulation of the results from a molecular beam experiment. A user running this program on a desktop machine can enter the relevant parameters for the computationally intensive calculation and run it from anywhere on the Internet using a machine at PNL. Once the calculation is finished, the results are sent back and displayed on a resizable, zoomable graph on the user's desktop. When the program is running, all of the network communication is taking place in the background, essentially invisible to the user, and the results appear within seconds rather than the many minutes that would be required if the calculation were taking place locally.

Publication

R. T. Kouzes, Editor. 1994. *Proceedings of the Workshop on a Collaboratory for Environmental Molecular Sciences*. Richland, Washington.

Computer Modeling of DNA Perturbations

John H. Miller (Biology and Chemistry)

Project Description

Molecular modeling techniques were used in this project to investigate the biological effects of radiation and chemical exposures. The minimum-energy conformation of DNA lesions was calculated by ab initio quantum-chemical methods, and classical molecular dynamics simulation was used to study the effects of these lesions on the structure of DNA oligonucleotides. Structure-function relationships derived by considering the interaction of damaged DNA with enzymes involved in replication and repair contribute to our understanding of the consequences of DNA damage at the cellular level and strengthen the scientific basis for assessing health risks of low-level exposure to radiation and chemicals in the environment.

Technical Accomplishments

Previous work on this project focused on oxidative damage to pyrimidine DNA bases and recognition of this damage by the base excision repair pathway. In FY 1994, focus was shifted to the cyclobutane thymine dimer that is a major DNA damage product of ultraviolet exposure. Earlier theoretical studies of perturbations to DNA structure by this lesion (Rao et al. 1984; Pearlman et al. 1985) came to dramatically different conclusions with one predicting significant bending while the other indicated much more subtle changes in DNA conformation due to dimer formation. Advances in computer technology allowed us to improve on the molecular-mechanics approach of these earlier studies by using molecular dynamics simulation to sample a larger region of conformation space and to treat solvation effects more accurately. In addition, recent nuclear magnetic resonance studies of the conformation of DNA containing a *cis, syn*-cyclobutane thymine dimer (Lee et al. 1994) provided the opportunity to compare our calculations with experimental data.

The methods applied in this study were similar to those developed to investigate the effects of ring-saturated pyrimidine lesions (see publications). A thymine dimer was placed in the duplex dodecamer $d(CGCGAA\underline{TT}CGCG)_2$ at the underlined position and molecular dynamics simulations were carried out in the presence of counterions and a box of water with periodic boundary conditions. Distortions of DNA structure produced by the lesion were localized near the 5' thymine of the dimer and included *syn* orientation around the glycosyl bond, reorientation of the base with respect to the helical axis, and weakening of hydrogen bonds. A wider minor groove in the vicinity of the lesions was also predicted by the calculations. The calculated H(1')A6 to H(6)T7 distance was 7 Å whereas all other H(1') to H(6) pyrimidine/H(8)purine distances were less than 5 Å. The H(1') to H(6) distance on the 5' thymine of the dimer is the only cross-peak of this type that was not observed in the experimental data of Lee et al. (1994) indicating a distance greater than 5 Å.

These studies of perturbations to DNA structure by thymine dimers also contributed to the understanding of how the repair enzyme T4 endonuclease V recognizes cyclobutane pyrimidine dimers. This enzymes binds to duplex DNA nonspecifically and undergoes one-dimensional diffusion along the double helix until it encounters a thymine dimer. Upon encounter with a dimer, T4 endoV binds more tightly and engages in enzymatic excision of the damage. The scanning mode of nonspecific binding requires an ionic strength below 50mM NaCl. This suggests that T4 endoV binding to DNA is sensitive to the counterion distribution around the double helix and perturbations of the native distribution may be a component of damage recognition. In our model calculations, that include counterions and water of hydration explicitly, incorporation of a thymine dimer into DNA leads to a reduction of the counterion concentration on the 5' side of the lesion. Work is in progress to further investigate this electronic mechanism of DNA-damage recognition by repair enzymes.

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Presentation

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Demand-Side Management Tool for Allocation of Water Resources

Duane A. Neitzel (Earth and Environmental Sciences)

Project Description

Recognizing the critical role that water plays as a fundamental resource for economic development and maintenance of economic vitality and witnessing the significant water shortages experienced in the Western United States over the last several years (especially on the Yakima River this summer), the project team explored options to satisfy ever growing water demands when faced with uncertain supply. Drawing on the experiences of the electric utility industry (in Demand-Side Management [DSM]), the project team applied demand-side management to water resources. The critical conceptual advancement in this effort is the idea that water allocation can be based on the services provided by water, not simply the quantity of water supplied to competing users.

Historically, water has been viewed as a means to economic growth, particularly in arid locations. Water has also been viewed as a renewable resource. Recent droughts, declining fish stocks, and significant decreases in the quality of both surface and groundwater are all signals that water is being used more quickly than the resource can be renewed. In other words, current water resources have been over-allocated. The Yakima River Basin, in Eastern Washington, yields a good example of the problems associated with the over-allocation of water resources.

The scope of this effort was to determine if the application of demand-side management principles to water could yield positive results. The challenge was to quickly develop a simple analytical method and identify data of sufficient quantity and quality to give us a reasonable answer. There are barriers and uncertainties to effective use of demand-side management for water allocation. They are discussed in this report.

Technical Accomplishments

The water needed to grow crops in the Roza Irrigation District was calculated two ways.

1. *Water Used as a Function of Crop Consumption Minus Effective Precipitation*

The crops grown and estimates of irrigated acres in the Roza District are identified in Roza (1992). Crops were combined into seven categories. The water consumed minus the effective precipitation (Cu-Ep) by each crop during a year was based on estimates of Cu-Ep (in acre inches) from the Richland and Prosser, Washington, areas. No estimates for Cu-Ep, specific to the Roza District, were found. We estimated the acre-feet of water required for each crop by multiplying the acres irrigated times the Cu-Ep and dividing by 12. Using this method, the total acre-feet of water required to grow crops in the Roza District is 156,553.

2. *Water Used as a Function of Water Application Techniques and Application Efficiency*

In the second method, we used the efficiencies of each type of water application system used in the Roza District and acres irrigated with each type of application system to estimate the water required to grow crops. The types of crops grown and the estimated acres were taken from Roza (1992). Three types of water application are used in the Roza District: furrow, corrugation, and sprinklers. Efficiency estimates (USDA 1985) range from 0.6 to 0.7.

The acres watered with each type of application system were estimated as follows. There are 59,070 acres of irrigated land in the Roza District. About 75% of the 30,805 fruit-growing acres is sprinkled. Roza (1992) states that 52% of the Roza District is sprinkled. Therefore, we estimate 1) that 30,716 acres of the Roza District are sprinkled, 2) 7,612 acres of the non-fruit growing acres are sprinkled, 3) 27% of the non-fruit acres are sprinkled, and 4) 73% of the non-fruit growing acres are irrigated by furrow or corrugation.

By multiplying the acres of a given crop times the estimated percent for the appropriate application type, we estimate the acres of each crop for each application type. The appropriate application types were taken from USDA (1985). Summing the crop-specific estimates for each category and dividing by the total acres for the crop category gives us the acre-weighted average mean efficiency for each crop category. Dividing this estimate by the percent of total acres for the category gives us a weighted efficiency for each crop category. The sum of these efficiencies then yields a total weighted efficiency. The total weighted efficiency times the amount of water delivered to the farms equals an estimate of the water needed to grow the crops in the Roza District. Using this method, the total acre-feet of water required to grow crops in the Roza District is 148,540.

Diversion, Waste, and Loss Estimates for Roza District—The last year that the Roza District received its total allocation of water was 1991. During the irrigation season, 378,240 acre-feet of water were diverted from the Yakima River at Roza Dam. About 48,000 acre-feet were wasted in the main canal. Waste is defined as the water required to operate the irrigation district in excess of the water required to deliver water to the lateral canals and individual farms within the district. About 61,000 acre-feet of water are lost. Loss is defined as the water that evaporates from or leaks out of the canal during delivery. Given these estimates, about 268,835 acre-feet of water are delivered to the lateral canals within the system. Waste and loss within the laterals is about 43,000 acre-feet per year. Total acre-feet of water delivered to the farms of the Roza District during 1991 was about 226,000 acre-feet.

This information was used to estimate the potential differences between current operations and potential operations using more efficient methods of application.

Acre-weighted mean efficiencies for crop categories and all crops were calculated for the best available allocation type in the same manner as we used for current applications. The best available water application efficiencies are 0.7 for sprinklers and 0.9 for trickle applicators (USDA 1985). The weighted-acre efficiency was then used to calculate potential differences for current diversion and on farm efficiencies depending on the type of on-farm water application used.

In 1991 (the last year that Roza received full allocation), the Roza District delivered approximately 226,000 acre-feet to the farms. The estimated crop requirements (the total amount of water required by the crops, less the effective precipitation) are about 150,000 acre-feet. This yields an existing on-farm efficiency of 66% (148,540/224,540). By changing the irrigation methods for each crop to the most efficient appropriate technology, the on-farm efficiency can be increased to 85% (148,540/180,071). This is an absolute savings of over 45,000 acre-feet, or 20% of the water delivered to the farms in 1991.

These savings were also examined in terms of instream flows. In 1991, approximately 378,000 acre-feet were diverted from the Yakima River at the Roza diversion dam. Because of non-linearity in the canal losses, the on-farm savings of 20% become a savings of 24%, or about 90,000 acre-feet at the diversion canal. This could represent an increase in instream flows of 275 ft^3/sec during the peak water use months of July and August.

Conclusion

When demand-side management principles are applied to water allocations in the Roza District, our analysis indicates that the same quantity and types of crops can be grown using less water than is currently used. The difference can be expressed as 45,000 acre-feet less water delivered to the farms (a 20% savings).

This difference has many potential "uses" within the basin. Possible uses are increased irrigated land, decreased numbers of years in which water allocations cannot be met, increased water for habitat and water quality improvements, and increased instream flows. Extensive analysis of the potential benefits was not included in this study.

Potential benefits will require resolution of some important uncertainties related to water allocation in the Roza District and elsewhere in the Yakima Basin. The key uncertainties relate to hydrological characteristics of the basin, socioeconomic constraints of changing water application techniques on the farms, and legal requirements for changing water use.

References

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U.S. Department of Agriculture (USDA). 1985. *State of Washington Irrigation Guide*. Prepared by Washington State University Cooperative Extension Service, Pullman, Washington for the USDA, Pullman, Washington.

Developing Capability for Global Studies to Anticipate Changes in Vegetative Cover

Norman J. Rosenberg (Global Environmental Management)
Edward J. Rykiel (Earth and Environmental Sciences)

Project Description

The Global Change Assessment Model is PNL's principal tool for analyzing the full complexity of global change issues including their societal, economic, and natural resource causes; their effects; and the interactions and feedbacks among these causes and effects. The research conducted under this particular project has contributed to the overall Global Change Assessment Model development by providing a capability for global scale modeling of changes in ecosystem boundaries and primary productivity in response to prospective changes in climate. Ultimately, we hope to access models capable of tracking changes in geography and productivity as a transient process including species succession. A two-step approach has been taken:

1. Acquisition of a working ecosystem model for immediate use in the Global Change Assessment Model development process and development of linkages for that model with other Global Change Assessment Model modules and with the Global Change Assessment Model GIS.
2. Search for more advanced models with the capability to simulate primary productivity and transient processes.

Technical Accomplishments

Computer code for a working ecosystem model (BIOME1) was acquired from Dr. Allen Solomon of U.S. Environmental Protection Agency's Corvallis, Oregon, laboratory. Software was developed at PNL/BWO to link BIOME1 with the geographical information system being developed for Global Change Assessment Model. First steps have also been taken to link BIOME1 to the Erosion Productivity Impact Calculator, our agricultural productivity module, and to HUMUS (Hydrologic Unit Model for the U.S.), our surface runoff and groundwater recharge module.

BIOME1 has been run for the United States under current climatic conditions with data provided by the University of East Anglia. East Anglia is a partner in the PNL Global Change Assessment Model development and is providing programs that map regional climate changes keyed to specific general circulation model sensitivities to greenhouse gas emissions.

BIOME1 now serves the Global Change Assessment Model as a "place-holder." The model provides information on the equilibrium geographical distribution of ecosystems as a function of climatic and soil conditions. The model does not, however, provide information on ecosystem primary productivity. BIOME2, a model under development at the University of Lund, Sweden, by Prentice and others, provides information both on provenance and productivity. At present, BIOME2 is also an equilibrium or steady-state model and does not deal with transient change. Work will shortly begin to develop a transient capability for BIOME.

Other Accomplishments

The approach was described at a U.S. Global Change Research Program briefing and at a meeting of the Social Sciences Research Council in Washington, D.C. in October 1994.

Development of a Chemical Carcinogenic Risk Calculation

Mary F. Jarvis, Timothy T. Jarvis, Peter J. Chamberlain, and Dennis L. Strenge (Earth and Environmental Sciences)

Project Description

The long-term objective of this project is to represent existing risk assessment programs in a relational database format program envisioned to be a user-friendly computation tool for professionals knowledgeable in the application of risk assessment. The finished program would be required to calculate chemical carcinogenic risk and/or toxicological risk to a human receptor, resulting from chemical contamination in the environment and/or the work place. The program will be useful to a large cross section of professionals including: environmental and/or industrial hygiene personnel at chemical plants, regulatory personnel, environmental consultants, and other risk assessors and/or risk managers. The work during FY 1994 covered the first phase of the project which resulted in preparation of an outline of the computer program and a phased approach to its development.

Technical Accomplishments

This initial phase of program development identified those risk assessment components that are and those components that are not suited for computer application. The natural limits of the proposed program were determined along with the development details of the proposed programming effort. Through this initial effort, it is apparent that substantial gains over existing risk assessment spreadsheeting programs, in speed or accuracy, will require highly sophisticated, state-of-the-art computer programming technologies.

An understanding of the component parts of producing a human health risk assessment report is required as the basis of the program structure. Each part can then be evaluated for suitability to computer implementation. The generalized steps in the development of a human health risk assessment report include

1. determination of chemicals of concern (COC)
2. development of a site conceptual model
3. exposure pathway/scenario determination
4. toxicity evaluation of chemicals of concern
5. source term verification for chemicals of concern (completeness of data set)
6. method and approach documentation
7. screening of chemicals of concern
8. evaluation of the chemical and physical properties of chemicals of concern
9. demography information
10. information on cultural traits
11. chemical transport modeling
12. chemical fate modeling
13. exposure modeling
14. risk calculation
15. determination of uncertainty
16. report preparation.

Computer programming requires standardization of the computational process, yielding high precision from one set of calculations to the next. Given that each environmental contamination site is unique, and a program is written which accurately represents the relationships between the variables at the site, then application of the same program on another site will likely result in inaccurate risk estimates, unless the program code is altered to reflect the new relationships. It may be concluded that reduction in scientific accuracy is inherent in any attempt to standardize the risk assessment procedure as in computer programming. This inverse relationship between standardization and accuracy can be dealt with in programming by understanding the accuracy and sensitivity relationship of each risk assessment component to standardization. Of the steps in the risk assessment process, some are sensitive to standardization, in regards to their accuracy, while other steps can be relatively insensitive if handled correctly. The components of a site-specific human health risk assessment can be divided into three categories, grouped as to their accuracy and sensitivity to standardization.

Category 1 - Highly Sensitive

Because the uniqueness of a site is captured within them, the development of the site conceptual model, and determination of exposure pathway scenarios are highly sensitive to standardization in regards to accuracy.

Components in the category include: determination of chemicals of concern; development of a site conceptual model; exposure pathway/scenario determination; source term verification for chemicals of concern (completeness of data set); method and approach documentation; and demography information, and information on cultural traits.

Category 2 - Conditional Sensitivity

If the uniqueness of the site (as captured by the site conceptual model and exposure pathway scenarios) can be transferred to input parameters, boundary conditions, and limits of environmental fate models, transport models, exposure models, and risk characterization calculations; then the accuracy and sensitivity of these steps can be reduced to acceptable levels.

Components in the category include: screening of chemicals of concern, chemical transport modeling, chemical fate modeling, exposure modeling, risk calculation, and determination of uncertainty.

Category 3 - Insensitive

To the other extreme is the dose response of humans to a known chemical insult, the dose-response curves of individual chemicals are independent of the site and so their accuracies are insensitive to standardization. Also in this category are the physical properties of the chemicals themselves, such as solubility, vapor pressure, ionic status, reactivity, and boiling point.

Components in the category include: toxicity evaluation of chemicals of concern, evaluation of the chemical and physical properties of chemicals of concern, and report preparation.

The proposed relational database program has three stages of development. Each stage provides full functionality to accomplish data analysis, contaminant screening, site conceptual model design, fate/transport modeling, intake/exposure modeling, and risk characterization. Sensitivity and uncertainty analyses can then be done for each of these functions and for the entire system. The staged versions differ in that additional developments in the system result in 1) more extensive expert systems support to each of the above functions, and 2) increased flexibility for the user to exchange/integrate default (included) models or software with user-provided models, commensurate with the level of complexity the user determines necessary (i.e., with assistance from an expert system).

To the extent practicable, the risk associated with human exposure from the following pathways will be included in the program: 1) ingestion of chemical contaminants in drinking water; 2) dermal contact with chemical contaminants in water (via swimming or bathing); 3) inhalation of volatile chemicals released during domestic use of contaminated water supplies (i.e., during cooking, showering, toilet flushing, hand washing, food preparation, and during operation of household appliances); 4) inadvertent ingestion of chemicals in contaminated soil, dust, or sediment; and 5) dermal contact with chemicals in contaminated soil, dust, or sediment.

Dynamics, Modeling and Redesign of Microbial Proteins

Rick L. Ornstein (Theory, Modeling, and Simulation)

Project Description

The primary objective of this project was to develop new strategies and capabilities for improving the fundamental understanding of microbial enzyme structure-function-dynamics relations under extreme physical (temperature) and chemical conditions (in nonaqueous solvents, extreme pH, in various salts). Acquiring such an understanding will lead to timely improvements of protein/enzyme functionality that may impact environmental bioremediation, renewable resource utilization for energy production and industrial feedstocks, and industrial processes under extreme conditions but with much less environmental impact, as well as design of new sensors and design of new materials that are biodegradable. The secondary objective was to use and develop computational methods for producing plausible three-dimensional models of protein structures for environmentally relevant enzymes isolated from microbes. Such structures will aid in the early interpretation of collaborative nuclear magnetic resonance structure determination efforts (at PNL); with NOEs in hand, restrained dynamics will then be performed, eventually followed by additional unrestrained dynamics. Such an iterative and coupled experiment-theory effort will lead to an understanding of the essential structure-function-dynamic relations and lead to opportunities for rational redesign to improve enzyme functionality.

Extremozymes

The primary purpose of this task was to study the underlying structure-function-dynamic relations of proteins that function under normal physiological conditions and those that function under extreme conditions. Once a fundamental understanding is achieved, we shall use these relationships to a) redesign a mesophilic enzyme into a thermophilic enzyme, b) redesign an enzyme that functions in an aqueous solvent into one that functions in a nonaqueous solvent, c) redesign an enzyme's functional optimum pH range from ~7 to high alkaline pH (>11), and d) be able to vary the salt conditions. Accomplishing these proof-of-principle goals will have broad biotechnological implications.

Rubredoxins are non-heme iron proteins of low molecular weight that occur in several anaerobic bacteria and are believed to participate in electron transfer reactions. The high resolution x-ray structure of four rubredoxins from mesophilic bacteria and one hyperthermophile have been reported, and a solution nuclear magnetic resonance structure for the hyperthermophilic rubredoxin. The thermostable protein is unaffected after 24 hours incubation at 95°C, while the mesophilic proteins are denatured after brief exposure to 80°C. Thus, rubredoxins provide an unusual opportunity to study factors responsible for extreme thermostability. We will perform molecular dynamics simulations at 25°C and 95°C on four mesophilic and the hyperthermophilic rubredoxins. We anticipate that we will uncover key structural and dynamic determinants of thermostability for this class of protein. We then will apply these fundamental principles to an important mesophilic bacterial protein, via a coupled-theory experimental study, to design a thermostable form.

X-ray crystal structures of mesophilic and thermophilic varieties of malate dehydrogenase have recently become available. This NAD-dependent dehydrogenase enzyme class converts 2-hydroxy acids to the corresponding 2-keto-acids. The primary sequence of the mesophile and thermophile with available x-ray structures are 55% identical. The mesophile is inactivated at temperatures above 50°C, while the thermophile is fully active at 90°C. These enzymes are relatively large; they occur as homodimers of approximately 67,000 daltons molecular mass with each subunit ranging from 326 to 333 amino acids with one NAD molecule per subunit. The malate dehydrogenase system because of available three-dimensional structures, clones, and mechanistic data, appears to be the best enzyme system to study in order to gain an understanding of enzymatic processes under widely varying temperatures. These dehydrogenases are about 13-fold larger than rubredoxin; making their study by simulation methods much more computationally demanding.

Water, while an ideal solvent for the predominantly polar reactions required for biotic processes, is a poor solvent for nearly all applications in industrial chemistry. Most organic compounds of commercial interest are very sparingly soluble and often unstable in aqueous solutions. Hence, industrial chemistry is based on organic solvent chemistry and has mostly ignored the potential benefits of highly selective and environmentally benign enzymic catalysts. Research during the last decade has demonstrated that some enzymes maintain considerable activity in nonaqueous solvents. Professor Klibanov and coworkers from Massachusetts Institute of Technology have demonstrated that at least some subtilisins are partially functional in nonaqueous solvents. The starting structures for our simulations are the recently published (Klibanov et al.) high-resolution x-ray crystallographic structures of subtilisin in anhydrous acetonitrile or in water. In FY 1994, we performed simulations to understand the structural and dynamic impact of nonaqueous solvents on subtilisin function. Efforts will continue in FY 1995. Such an understanding is expected to aid in the rational redesign of enzymes with properties optimized for specific nonaqueous solvents.

Salt concentrations and types vary widely in the environment and in polluted sites. If proteins and enzymes are to be of direct use in such environments, the effects of varying salt conditions must be understood in order to open the way for potentially necessary redesign for protein/enzyme stability and functionality under such conditions. The structure of Bence-Jones protein, two covalently linked immunoglobulin light chains of about 450 amino acids (total), has been solved by x-ray crystallography under a variety of conditions including very recently under a range of salt concentrations and types. Unexpected structural changes and dynamic changes were noticed in the crystal structures recently obtained by Dr. Marianne Shiffer and coworkers at Argonne National Laboratory. This system is ideal for uncovering the basis of salt effects of proteins via a coupled experiment-theory approach.

PNL Enzymes: Modeling, Simulation, and Redesign

For every different protein with an available three-dimensional structure, there are about a thousand sequenced proteins with no known structure. This situation is likely to get worse as sequencing methods improve. Thus the secondary purpose of this task is to assemble and develop state-of-the-art computational methods to assist in protein/enzyme structure determination at PNL and to perform subsequent rational redesign. These capabilities will functionally include a) predicting three-dimensional structure by homology modeling prior to any knowledge of experimental three-dimensional structure, b) refining three-dimensional structure as nuclear magnetic resonance NOEs become available, c) performing long-time molecular dynamics simulations on the nuclear magnetic resonance-determined three-dimensional structure without any restraints, and d) obtaining structure-function-dynamic relations in order to perform rational redesign.

Homology modeling of a new sequence can often lead to a useful preliminary three-dimensional model, which may be of considerable value during the early phases of structure determination by solution nuclear magnetic resonance. During later steps of three-dimensional structure determination, an NOE-restrained simulation protocol will be useful for obtaining a more accurate three-dimensional structure. After the structure is determined by nuclear magnetic resonance, additional long dynamics simulations without NOE restraints is of value in gaining a deeper understanding of dynamic fluctuations and transients. We will apply such methods to proteins obtained as part of this project in order to understand the fundamental structure-function relations and to perform rational redesign. Preliminary steps were taken to develop a coupled experiment-theory effort to obtain the three-dimensional structure of bacterial dehalogenases (i.e., tetrachlorohydroquinone reductive dehalogenase).

Technical Accomplishments

Several 200-psec molecular dynamics simulations of the protein rubredoxin with a 10Å shell of water were completed. Simulations were performed at room temperature on the hyperthermal form and various mesophilic forms. Simulations are under way at 95°C.

Dr. Zheng began initial simulation efforts on the enzyme subtilisin in aqueous and nonaqueous solvents. With respect to the subtilisin studies, Professor Klibanov has agreed to present a seminar at PNL—Professor Klibanov pioneered the field of nonaqueous enzyme catalysis and recently published the first enzyme x-ray crystal structure in neat organic solvent and compared it to the structure in aqueous solvent (subtilisin). A possible collaboration is in the works.

The Bence-Jones protein system was chosen as an ideal system to study the effects of varied salt concentration and type on protein structure and dynamics in view of the recent series of x-ray crystal structures solved in the laboratory of Dr. Schiffer, Argonne National Laboratory. We are collaborating with Dr. Schiffer in this effort.

Preliminary steps have been taken to develop a coupled experiment-theory effort to obtain the three-dimensional structure of bacterial dehalogenases (i.e., tetrachlorohydroquinone reductive dehalogenase). This enzyme has been isolated and purified by Luying Xun while Michael Kennedy is attempting to determine the structure using solution nuclear magnetic resonance methods. It is anticipated that this effort will lead to a fundamental understanding of the underlying structure-function-dynamic relations and subsequent rational redesign.

Other Accomplishments

A postdoctoral, Dr. Ya-Jun Zheng, joined the project on April 18, 1994, from University of California, Berkeley.

Effect of Microbial Biofilm on Sorption in Sediments

Cheryl D. Gullett and James E. Szecsody (Earth and Environmental Sciences)

Project Description

This study was initiated to examine microbial attachment (microscopically) on mineral surfaces and conduct a set of controlled experiments on a single sediment to compare adsorption of Co(II) in a mixed system of bacteria and sediment to that on the sediment only. The sediment used in this study was a synthetic 0.6% iron oxide-coated sand that has been extensively characterized in other studies. The bacterium used in this study was a subsurface endospore-forming bacterium designated G-8013 (see Figure 1). Co(II) adsorption to sediment only was examined under varied geochemical conditions likely to be important in field systems (i.e., Co(II) concentration, pH, time). Co(II) adsorption to microbes was examined under varied geochemical (Co(II) concentration, time) and microbial conditions (microbial concentration, time). Finally, Co(II) adsorption to both sediment and microbes was examined in systems in which the Co(II) concentration, microbe concentration, and time was varied. Adsorption was modeled in individual sediment and microbe systems and used to predict adsorption in the coupled system.

Figure 1. Photomicrograph of G-8013, an endospore-forming bacterium isolated from the subsurface at Hanford. This filamentous bacteria binds Co(II) as well as covers absorptive sites on sediments, altering fluid transport behavior and contaminant adsorption. At high microbe concentrations, Co(II) adsorption is less than the sum of adsorption to both sediment and microbes because of a coupled effect such as microbes covering mineral surface area and decreasing the mass of adsorption to the mineral surface. Scale bar = .03 mm.

Technical Accomplishments

Co(II) adsorption to the sediment at different Co(II) concentrations (Figure 2a) was nonlinear and indicated a maximum number of surface adsorption sites (by the decrease in adsorption at high concentrations). The adsorption at low concentrations was also not linear, and indicated adsorption to more than one mineral surface. Microscope and chemical analysis of the surface from other studies indicated that adsorption is predominantly to iron oxides with some contribution of other mineral surfaces. A Langmuir-Freundlich (multi-site) model was fit to the data (shown in Figure 2a). The pH adsorption edge (not shown) also indicated generally adsorption to one surface type. Time-course experiments indicated that Co(II) adsorption was relatively fast and reached equilibrium within an hour.

Co(II) adsorption to microbe G-8013 was considerably greater than that on sediment (approximately 6 orders of magnitude on a per gram basis). Adsorption to microbes at different Co(II) concentrations (Figure 2b) was also nonlinear with less adsorption at high concentration, although a maximum number of adsorption sites is not as clearly definable as with the sediment. Time-course experiments indicated that adsorption was fast (within minutes). At high Co(II) concentrations, adsorption decreased over several hours, possibly indicating toxic effects. The Langmuir-Freundlich model fit to microbe adsorption data (shown in Figure 2b) had a similar slope to the sediment adsorption data at low concentration.

Co(II) adsorption in coupled water-sediment-microbe systems was compared to predicted adsorption assuming that adsorption to the sediment is independent and additive to adsorption to the microbes (solid line in Figure 2c). Results at a microbial concentration of 10^6 CFU mL^{-1} (Figure 2c) show that adsorption in the coupled system was less than that predicted. This may be caused by microbial coverage of the mineral surface, although the microscopic examination of the surface was inconclusive. Because the calculated monolayer coverage of microbes is considerably greater than the mineral surface area, microbial coverage of the mineral surface is feasible. At different microbe concentrations (data not shown), adsorption to microbes was insignificant at less than 10^6 CFU mL^{-1}, so Co(II) adsorption was nearly all to the sediment.

Results are intuitive; at low microbe concentrations, Co(II) adsorption to microbes is insignificant and microbes do not cover mineral surfaces. At high microbe concentrations, Co(II) adsorption is less than the sum of adsorption to both sediment and microbes because of a coupled effect such as microbes covering mineral surface area and decreasing the mass of adsorption to the mineral surface.

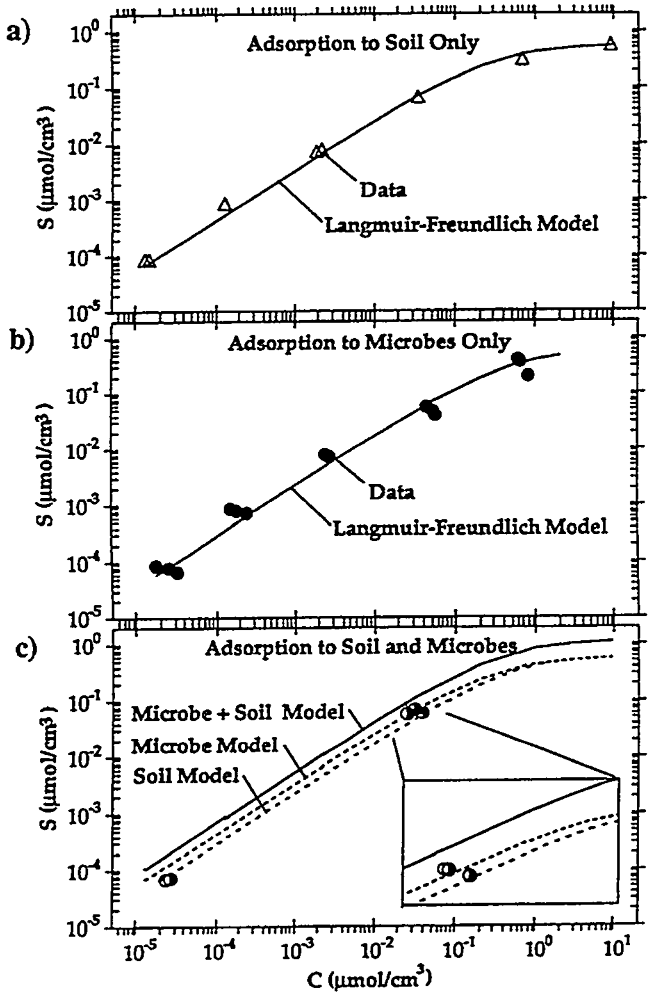

Figure 2. a) Co(II) adsorption to iron oxide-coated sand at different Co(II) concentrations, b) Co(II) adsorption to microbes G-8013 at different Co(II) concentrations, and c) Co(II) adsorption to both microbes and sediment. Lines in a) and b) are Langmuir-Freundlich model fits to data and solid line in c) is the predicted adsorption response in the microbe-sediment-water system.

Elastic Properties, Solution Chemistry and Electronic Structures of Oxides, Silicates and Carbonates

Anthony C. Hess (Theory, Modeling, and Simulation)

Project Description

The first-principles calculation of the equations of state (EOS) and elastic properties of oxides and sulphides were done. The results are being used to develop a new approach to understanding and predicting the solid-solution chemistry of these phases. This work may suggest new materials that could immobilize radioactive waste. This work is also assessing the reliability of emerging theoretical methods being applied to the study of mineral surfaces. Such an assessment is needed to provide a foundation for theoretical work pertaining to environmental geochemistry. Finally, the investigations of hydroxide phases will provide insight on the crystal chemistry of hydrogen in minerals. This is needed to understand how water affects the behavior and stability of glasses used to contain radioactive waste.

Technical Accomplishments

During FY 1994, work concentrated on the application of density functional calculations to iron bearing phases. The scope of the project was extended to transition metal sulphides at the expense of carbonate phases. The practical application of density functional theory to atoms, molecules, and solids has traditionally required using the local density approximation (LDA) for the exchange-correlation potential. The local density approximation, however, gives an inadequate description of metallic iron, iron oxides, and iron sulfides. In the local density approximation, the exchange energy is underestimated and the correlation energy is overestimated. In recent years, extensions beyond the local density approximation known as the generalized gradient approximation (GGA) have been developed by Perdew and coworkers. The generalized gradient approximation functional was added to the full potential linearized augmented plane wave (FLAPW) method and applied to various iron oxides and sulfides. The generalized gradient approximation functional gives a substantial improvement relative to the local density approximation—enough to allow reliable predictions of the stabilities and equations of state of iron phases.

High-Pressure Phase Transitions of FeO

Shock-wave compression experiments on FeO show a phase transition near 70 GPa and T > 1200K. The nature of this phase transition has been unknown but has inspired much speculation in the geophysical literature.

We determined the static free energies and equations of state of FeO in the B1 (ideal NaCl), rhombohedrally distorted antiferromagnetic B1, ferromagnetic B2 (CsCl), and ferromagnetic B8 (NiAs) structures. We used the FLAPW method beyond the local density approximation. The generalized gradient approximation for the exchange-correlation functional appears to give an accurate description of FeO as the equation of state and ground state structure are predicted correctly. The static ground state of FeO is predicted to be antiferromagnetic with a rhombohedrally distorted NaCl structure. The rhombohedral distortion increases with pressure. The B8 (NiAs structure) phase is stable relative to the B2 (CsCl) structure for all pressures below 200 GPa*. The high-pressure, high-temperature phase of FeO, therefore, is argued to be FeO with the B8 (NiAs) structure. The structure differs from the ideal NiAs in that the c/a ratio is 1.9 (0 GPa) and increases to 2.2 (150 GPa). The static transition pressure from the rhombohedral FeO phase to the B8 (NiAs) structure is predicted to be near 125 GPa. If this transition is that occurring near 70 GPa and T > 1200K under shock compression, then the Clapeyron slope must be at least -0.046 GPa/K. From the 70 GPa volume change of -0.1 A3/mol FeO, we predict that the entropy change is 2.7 J/mol-K.

High-Pressure Phase Transitions of FeS

FeS undergoes a high-pressure phase transition to a paramagnetic phase near 16 GPa. The nature of the electronic structure change and the high-pressure structure of FeS have been unknown. FLAPW calculations on FeS give the correct ground state structure (NiAs). Of great theoretical interest is that the magnetic moment of FeS disappears under small compression. In the traditional ligand field theory view, this would be interpreted as a spin-pairing transition. This would cause FeS to become a diamagnetic insulator. However, the high-pressure electronic structure corresponds to a metallic Pauli paramagnet. The high-pressure structure of FeS is a distorted B2 (CsCl structure).

Electronic Structures of Spinel Oxides and Sulphides

In collaboration with Andrew Gibson, we began work on the electronic structures of Fe_3O_4 and Fe_3S_4 spinel phases using the FLAPW method.

Publications

D. M. Sherman. "The Stability of Possible Fe-FeO and Fe-FeS Alloys at High Pressure and the Composition of the Earth's Core." *Earth and Planetary Science Letters* (in press).

D. M. Sherman and H.J.F. Jansen. "The High Pressure Phase of FeO." *Geophysical Research Letters* (in press).

Electrolyte Diffusion: Molecular Dynamics and Transport Modeling

James R. Rustad, Andrew R. Felmy, and Carl I. Steefel (Earth and Environmental Sciences)

Project Description

The objective of this project was to develop the capability of predicting the effects of multicomponent diffusion in diffusion-dominated waste disposal regimes using computational molecular dynamics methods and to develop thermodynamical and continuum mechanical computer models to take account of multicomponent diffusion effects on breakthrough times.

Technical Accomplishments

In FY 1994, we

- assembled a computer code implementing a thermodynamical/continuum mechanical model to calculate diffusion profiles
- performed a literature review and compiled a database of experimental results on diffusion in multicomponent electrolytes
- performed a literature review on the possibilities of using time-saving approximations in molecular dynamics simulations of electrolytes (nonequilibrium molecular dynamics, brownian dynamics, and integral equation methods)
- obtained a molecular dynamics code (SOLVENT) which can be used to efficiently simulate electrolyte solutions, modified the code, and initiated molecular dynamics calculations on Na-Sr-Cl-H_2O liquids
- performed modifications to a molecular dynamics model for water, which allows calculations to be carried out on hydroxide ions.

Because of the large computational demands of performing molecular dynamics simulations on electrolytes at approximately 1 million concentration with explicit water molecules present in the simulation, we initially searched the literature for examples of calculations in which the solvent molecules are projected out of the simulation. We found that while these kinds of calculations can be of qualitative value, these methods lacked sufficient decided that explicit solvent calculations were necessary to the success of the project. We then obtained a molecular dynamics code (SOLVENT) which is set up to do molecular dynamics calculations on electrolytes. We modified the code to deal with ternary electrolytes and initiated calculations on the Na-Sr-Cl-H_2O system for which off-diagonal cross-coupling is fairly strong and for which there are experimental data over a range of compositions. Due to the vast amount of computational resources necessary for these calculations, the calculations are still being performed.

We determined through approximate calculations using thermodynamical/continuum mechanical code that hydroxide ion was the most likely component to provide a sufficiently strong coupling to problem anionic contaminants, such as pertechnetate ion, to be used in engineering a diffusion barrier to contaminant migration. Because the physical process for diffusion of hydroxide involves the dissociation of water, we began investigating the possibilities of using dissociating water models in molecular dynamics simulations of electrolyte diffusion. To ensure that the model for the production of hydroxide ion in aqueous solutions was performing adequately, we performed molecular dynamics simulations of the hydrolysis of ferric iron and orthosilicate anion in aqueous solution.

Publications

J. R. Rustad, A. R. Felmy, and B. P. Hay. "Water clusters using parameterized potentials." (in preparation).

J. R. Rustad and B. P. Hay. "Molecular dynamics simulation of silicic acid and orthosilicate anion in aqueous solution." *Geochim et Cosmochim. Acta* (in press).

J. R. Rustad, B. P. Hay, and J. W. Halley. "Molecular dynamics simulation of iron(III) and its hydrolysis products in aqueous solution." *J. Chem. Phys.* (in press).

Environmental Catalysis

Anthony C. Hess (Theory, Modeling, and Simulation)

Project Description

The objective of this work was to gain a better understanding of the influence of surface geometry and electronic structure on the reactivity/selectivity of heterogeneous chemical catalysts. Special emphasis was placed on identifying and subsequently understanding the surface chemistry of environmentally important catalysts capable of remediating chemical waste.

Technical Accomplishments

During the past several years we have carried out investigations into the surface properties of many metal oxides and aluminosilicates. These studies have demonstrated that modern theoretical tools can make substantial contributions to understanding the systems of interest and actively participate in a rational redesign phase of a material surface. Historically, many of the materials we have studied are important industrial catalysts with several being the material of choice in waste reduction processes (the most frequent use is for emission abatement). The current generation of catalysts capable of selective reduction or oxidation of reactants frequently relies on the use of very expensive (frequently toxic) second and third row transition metal atoms as promoters. The high cost of this class of metal promoters frequently drives the end-user cost of devices relying upon them to intolerable levels. One approach in the redesign (or perhaps rational design) of a catalyst is to first understand precisely what aspect of the total catalyst system is responsible for the observed catalytic activity. Once this is determined, modifications of the critical aspects of the material can be undertaken, resulting in a new material, the properties of which are judged for their commercial value. Although the full-scale redesign of catalysts is still a few years into the future, we have been able to outline a working framework for such efforts to proceed and have performed work designed to demonstrate the feasibility of using today's technology to solve the initial phases of this complex problem. The initial aspects of a catalyst redesign strategy involve understanding the detailed interactions of a reactant with its external surfaces (which may include topological and point defects, promoters, inhibitors). This is an enormously complex problem which has proven to severely stress modern experimental and theoretical techniques. The principal difficulties from the point of view of theoretical methods involve not the accuracy of current methods but the cost and the length of time it takes to obtain a satisfactory solution. Experimentally, the difficulty lies in controlling the synthesis of interesting materials at the atomic level and developing techniques which yield atomic information on critical observable for insulating systems.

Our approach consisted of a tightly focusing experimental techniques and theoretical methods on the same problem set with the goal of understanding oxide surface structure, speciation, and reactivity. It should be realized that neither approach (experiment or theory) alone can provide all of the required information on the system of interest. As an example, the best experimental measurements may provide information on the binding energy or vibrational spectra of species on oxide surfaces, but typically yield little to no data on the structure. Equivalently, high quality theoretical calculations will yield both structural and energetic data but even the most sophisticated theories require experimental validation. Our approach has been to evaluate the theory on a per system basis by establishing its correspondence to experimental measurements on key observable common to both approaches. This could be done, for example, by comparing theoretical results with the empirical measurement of the coverage dependent binding energies and/or vibrational spectra and allowing the theory to predict the detailed geometries of the active site. In addition, we plan to evaluate the role of surface defects in influencing overall catalytic properties. In this way confidence is gained in the theoretical method and information can be obtained, which is difficult if not impossible to obtain experimentally. This is an essential first step in understanding the catalysis of these materials as it provides a determination (in fact a definition) of what the catalyst is at an atomic level. Our initial success in this project indicates to us that, even given the limitations of today's technology, if all appropriate methods are focused on a system of interest, enough information can be obtained for a coherent picture of the structure and chemistry of that system to emerge.

During the past year we have continued to focus upon the surface chemistry of multiple faces of ZnO, MgO, and α-Al_2O_3. These materials have been chosen for study based upon considerations such as, a) the type and quality of available experimental data, b) the materials known ability to function as active catalysts (e.g., polar faces of ZnO), or c) all are commonly used as a support for metal promoters on their surfaces. To begin to understand methanol formation reactions, we have studied the interaction of CO and H_2O on the non-polar faces of ZnO with and without the presence of Cu promoter atoms. These studies are allowing us to understand the details of the substrate promoter atom interaction. In addition, our work on α-Al_2O_3 has resulted in an increased understanding of the surface structure of this compound and has stimulated work related to the synthesis of ultrathin films of this material. Recently such films, when acting as supports of various metal atoms, have been demonstrated to possess desirable catalytic properties. Our studies of MgO have centered upon understanding the effect of various topological defects on the reactivity and kinetics of simple precursor reactions on this surface. Simple structural defects can have a marked effect on the observed chemistry. For example, we have shown that low coordination sites, such as corner defects, can chemi-dissociatively adsorb water without an energy barrier. Results such as these can be used in part to help quantify the presence (or perhaps even number density) of such reactive sites on the surfaces of these and related materials. We have also carried out investigations of structural aspects of the acid sites in simple zeolites, as well as the interaction of charge neutral species with frameworks of these materials.

Publications

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Enzymology of Bacterial Metal Reductase and Dehalogenase

Yuri A. Gorby and Luying Xun (Environmental Microbiology)

Project Description

This project included two principal tasks. The objectives of the tasks were to identify the genes that encode for metal reducing enzymes in a dissimilatory Fe(III)-reducing bacterium and elucidate the enzymological pathway for anaerobic reductive dehalogenation in *Desulfomonile tiedjei* DCB-1. The information obtained from this work is necessary for developing models that predict and evaluate the fate of metal contaminants in environments populated with metal-reducing bacteria and for developing novel bioremediation processes for chlorinated organic contaminants. Additionally, the results are vital for designing and operating bioreactors that remove contaminants from industrial waste streams and for designing molecular probes as monitoring tools for in situ bioprocesses.

Technical Accomplishments

Enzymology of Bacterial Metal Reductases

Metal reducing bacteria couple the oxidation of reduced organic matter or hydrogen to the reduction of multivalent metals (e.g., iron, manganese, chromium, uranium, and chelated forms of cobalt). As natural inhabitants of anoxic aqueous, sedimentary, and subsurface environments, these organisms can directly influence the environmental fate of anthropogenic or naturally occurring heavy metals and radionuclides. Recent scientific effort has focused on understanding the implications of these bacteria to natural biogeochemical processes and how these bacteria can be exploited in remediating contaminated environments and contained process waste streams. However, little is known about the mechanism of microbial metal reduction and the distribution of metal-reducing bacteria in natural environments.

Two approaches were taken to identify the genes involved in metal reduction by the dissimilatory Fe(III)-reducing bacterium strain BrY. The general strategy of the genetic approach required generation of mutants of BrY that lack the genes that encode for metal reductase(s), construct a genomic library from wild type BrY, move this library into the mutant BrY culture, and select colonies that contain library clones that complement the defect. The second approach required isolation and purification of the metal reductase enzyme directly, obtaining a partial sequence of the amino acid structure, and then synthesizing a molecular probe that would be used to identify the gene that encoded for the enzyme.

During FY 1994, mutant strains of BrY were generated, a genomic library of wild type BrY was partially constructed, and a metal reductase complex from BrY was purified. A majority of the 60 or more mutants generated by chemical mutagenesis contained mutations that restricted the flow of electrons to the metal reductase, but contained active forms of this enzyme. Two of the mutants, however, were defective in their ability to synthesize hemes for functional c-type cytochromes that are believed to serve as the terminal metal reductase enzyme. The defective genes will be identified by the method described above using the genomic library that is currently being constructed.

A metal reductase complex was purified from strain BrY by a series of physical separation and liquid chromato-graphic techniques. A six-protein complex containing hydrogenase, a single-type cytochrome, and H2-dependent Fe(III), Co(III), and Cr(VI) reductase activity was purified by ammonium sulfate precipitation of the soluble cell fraction followed by gel filtration chromatograph.

In the proposed model for the H2-dependent metal reductase complex in BrY, electrons are passed from H2 to menaquinone (Mq) through hydrogenase. Menaquinone then donates the electrons to a c-type cytochrome that may serve as the terminal metal reductase.

Fe(III), Co(III), and Cr(VI) reductase activities and heme content showed similar fold purification and percent recoveries. The c-type cytochrome in the purified complex was reduced by H2 only in the presence of menadione and was reoxidized by Fe(III), Co(III), or Cr(VI). These results demonstrated that a single enzyme is responsible for reduction of these metals and that cytochrome c is directly involved in metal reduction. The metal reductase complex also reduced insoluble Fe(III) minerals (e.g., amorphous Fe(III) oxyhydroxide, goethite, and hematite) that are common in natural environments.

Identification, Purification, and Characterization of the Reductive Dehalogenase of Desulfomonile tiedjei *DCB-1.*

Reductive dehalogenation is one of the promising anaerobic bioremediation techniques in the removal of halogenated compounds from the environment. The key enzyme involved in this process is reductive dehalogenases. *Desulfomonile tiedjei* is the only anaerobic bacterium in pure culture capable of reductive dehalogenation of halogenated aromatic compounds. The dehalogenase system in this organism is believed to be linked to its energy metabolism. The overall objectives of this project were to identify, purify, and characterize the reductive dehalogenase system of *Desulfomonile tiedjei* DCB-1 and to clone and sequence the corresponding genes. We used both biochemical and molecular biological techniques to characterize the reductive dehalogenase system of *Desulfomonile tiedjei* DCB-1. The knowledge gained from this study enabled us to develop a model system for reductive dehalogenation by anaerobic microorganisms and will facilitate designing effective bioremediation methods for halocarbon removal.

Efforts to purify the dehalogenase in several other laboratories had been unsuccessful. However, with intense effort, we successfully identified and purified this important enzyme. Our results are summarized below:

- *D. tiedjei* was successfully induced to dechlorinate 3-chlorobenzoate to benzoate in our medium, which gave higher cell yield than the reported medium did.

- Assay mixture for the dehalogenase was worked out, and the enzymatic activities of the dehalogenase were detected in the assay mixture containing the cell-free extract prepared from the induced cells.

- The active cell-free extract was further fractionated into soluble fraction and particulate membrane fraction by ultracentrifugation. The dehalogenase activity was found in the membrane fraction only.

- The membrane fraction was solubilized in a special buffer system containing a mixture of detergents (1% triton X-100 and 6 mM CHAPS). This buffer allowed us to recover about 10 to 20% of the dehalogenase activity originally present in the membrane.

- The dehalogenase enzyme was purified by a combination of several column chromatographic techniques (including an anion exchange column and a hydroxylapitate column).

- The dehalogenase consisted of two subunits with molecular weights of about 55,000 and 40,000 daltons, respectively.

These results will eventually allow us to completely characterize the dehalogenase and identify its mode of action. With the pure enzyme, we can also go on to clone the gene by using oligonucleotide probes designed from the N-terminal amino acid sequences, and to carry out other proposed tasks.

Publication

F. Caccavo, Jr., Y. A. Gorby, and M. J. McInerney. "Purification of the Metal Reductase Complex in the Dissimilatory Metal-reducing Bacterium Shewanella alga, Strain BrY." *Applied and Environmental Microbiology* (submitted).

Other Accomplishments

Margaret F. Romine was hired at PNL as a molecular biologist.

Shuisong Ni was hired as a postdoctoral associate.

Evaluation of DNA Fingerprinting of Salmonids

Duane A. Neitzel and William V. Mavros (Earth and Environmental Sciences)

Project Description

The use of individual genomic DNA fingerprinting as a method of marking provides for a very sensitive, natural, nonintrusive, and cost-effective way to manage salmonids in the Columbia River basin; however, the methodology is currently not feasible or available at Pacific Northwest Laboratory. A significant amount of effort has been invested into genetic identification of fish; however, there is a need for better resolution of fish populations than is currently available. DNA fingerprinting is a very powerful assay tool that can be used to nonintrusively identify individual salmonids. This technique has been validated by correctly identifying and matching tissue samples among a group of genetically similar chinook salmon.

In spite of concerted management efforts, the abundance of many Pacific salmon species is substantially below historical levels (Nehlsen et al. 1991). A number of programs have begun, throughout the Columbia River basin to meet the Columbia River Basin Fish and Wildlife Program (NWPPC 1987), in an effort to double the number of anadromous salmonids in the basin. An important strategy in the program is the use of artificial propagation to increase the number of naturally spawning salmon and steelhead. Recent reviews by Miller et al. (1990) and Waples et al. (1991) indicate that there are still substantial gaps in our knowledge of how to supplement natural populations effectively. Among the most important factors to consider is the genetic consequences of releasing artificially propagated fish into the wild. Artificially propagated fish may be ill-suited to the wild environment and hybridization may cause a reduction in fitness of the native stock through outbreeding depression. Fisheries managers can reduce these possible adverse effects by using a stock for outplanting that are genetically identical to the natural stock being supplemented. Therefore, it is important to have a method of assessing the nature and extent of genetic changes that occur as a result of supplementation. A genetic monitoring program will provide the best opportunity for determining whether the supplementation program 1) replaced the native gene pool with hatchery fish, 2) caused integration of native and hatchery stocks, or 3) resulted in the loss of the native gene pool.

Currently, most of the genetic monitoring programs use protein electrophoresis for isozymes analysis. Protein electrophoresis cannot be used to accomplish the complex objectives outlined above. New developments in using the DNA fingerprinting assay for human forensic and medical science have provided technology that can be used to solve fisheries problems (Gill et al. 1985; Jeffreys et al. 1985; Thein et al. 1986). DNA fingerprinting has immediate and wide-ranging applications to aquaculture and fisheries biology (Wright 1992). Traditionally, genetic identification by fisheries biologists has been limited to protein electrophoresis and mtDNA analysis (Nielsen 1992). These methods are still valuable for some aspect of stock identification but they have unacceptable disadvantages such as 1) often requiring the sacrificing of animals, 2) technically complex results and difficulty in interpretation of the results, and 3) information is usually limited to groups, not individuals. The new DNA fingerprinting assay can assist in the determination of quantitative genetics studies of salmonid species. The advantage of DNA fingerprinting assay over isozyme or mitochondria DNA is that DNA fingerprinting is individual specific. An important consideration for the maintenance of broodstock is that only small tissue samples, such as a few drops of blood or a fin clipping, are required for fingerprinting thus eliminating the destructive sacrificing of the whole fish.

Since DNA fingerprinting is in its infancy, development of DNA probes for species-specific application is still required as is the validation in their use among different salmonid species.

Technical Accomplishments

DNA fingerprints from six pairs of adult chinook salmon, *Oncorhynchus tshawytscha*, were determined and used as references. Tissues obtained from randomly selected offspring of each of the parental crosses were coded and subjected to a double-blind DNA fingerprinting analysis. We used a probe that gave the best definition and resolution of genetic patterns specific to chinook salmon DNA. Parental identification of each offspring was determined and compared to the mating records.

The use of a DNA fingerprinting assay to differentiate among chinook salmon individuals was validated in this LDRD experiment.

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Fourier Transform EPR Studies of Radiation-Induced Structural Alteration of DNA

Michael K. Bowman (Macromolecular Structure and Dynamics)

Project Description

The objective of this project was to use Fourier transform electron paramagnetic resonance (EPR) techniques to study the free radicals generated in DNA by ionizing radiation and chemicals. Initial work concentrated on two important areas of interest in DNA damage: locally, multiply damaged sites (LMDS) and the transport of electrons and holes from the sites of their initial production near DNA. This electronic conduction could be an important modifier of the initial pattern of damage that must be dealt with by the cell's repair machinery.

Technical Accomplishments

Cells contain efficient repair mechanisms to prevent damage to DNA by chemicals or ionizing radiation from causing any deleterious effects to the organism. Normal oxidative from aerobic metabolism is estimated to cause approximately 10,000 alterations to the DNA in human cells every day. Yet, this damage is repaired rapidly and efficiently. Cells that lack the ability to repair this damage exhibit extreme health effects as a result of the unrepaired damage. Perversely, ionizing radiation produces much the same spectrum of damage as the oxidative stress but causes serious health consequences at far lower levels of damage.

There must be some qualitative difference between the damage caused by ionizing radiation and that caused by oxidative stress. The current hypothesis is that the inhomogeneous distribution of the initial ionizations produces clusters of damage called LMDS, some of which are more difficult to repair and give rise to many of the biological consequences of radiation. Although there is much experimental evidence for the existence of LMDS, little is known about their exact spatial extent and composition. This is because of the uncertainties in the distribution of the initial deposition of ionizations, the extent of recombination of ions, and the mobility of the ions before they are chemically fixed and become more or less immobile.

We attempted the direct measurement of the LMDS parameters using Fourier transform EPR. The excitation of the entire EPR spectrum produces an effect known as instantaneous spectral diffusion that increases the phase relaxation of the EPR signal. This instantaneous diffusion component provides a direct measure of the dipolar field caused by other free radicals in the LMDS. Thus, it offers an opportunity for the direct measurement of the free radical component of the LMDS in frozen samples of DNA where mobility of the free radicals is suppressed.

Samples were prepared and irradiated. The instantaneous diffusion measurements were performed at different points in the EPR spectrum. The signals exhibited one component that showed no evidence of instantaneous diffusion and a second that did. The instantaneous diffusion coefficient was about 0.4 MHz and varied by a factor of two across the EPR spectrum. At the radiation doses used, the value of 0.4 MHz is much larger than it would be were the free radicals to be randomly distributed throughout the sample. This is a clear indication that LMDS in the irradiated DNA are reflected in the free radical distribution. In addition, the absence of radicals derived from the water shows that free radicals produced in the hydration layer is apparently quantitatively transferred to the DNA.

The observation of two components in the instantaneous diffusion measurements is a consequence of a limited number of free radicals in the LMDS. Thus, at some points in the EPR spectrum, only the observed radical in the LMDS is excited and thus, there is no instantaneous diffusion recorded. We are currently developing methods to take into account the partial excitation of the spectrum to yield both the number and the size of the LMDS.

We also have devised two new pulse sequences that are expected to reveal the EPR spectrum of the pairs of radicals in the LMDS. If they prove to be successful, they will correlate the spectra of the radicals in each LMDS. These experiments may indicate the extent of diffusion of the radicals on the DNA both before thermalization and trapping and as the result of thermal annealing. These experiments should provide data for comparison with and calibration of computer modeling of damage in DNA.

Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy Data Acquisition and Modeling

Richard T. Kouzes (Computing and Information

Project Description

The objective of this project was to develop advanced computerized analysis techniques for Fourier transform ion cyclotron resonance mass spectroscopy (FTICR-MS). Extensive computer simulations of the instrument were carried out to allow the greatest gain in system performance.

Ion cyclotron resonance has been exploited for many years to perform precision mass measurements. Most recent efforts in the area of FTICR-MS have concentrated on developments for measuring organic compounds or specific masses. Improvements in magnet and computer technology have allowed these broad range instruments to obtain resolutions in selected cases to better than one part in 10^8 (in energy units, 1 keV at 100 u). The objective of this research is to develop computer instrumentation analysis and methods which will allow FTICR-MS instruments to perform measurements of masses at the 100 eV (1 part in 10^9) level of accuracy. The ability to obtain such high accuracy over a broad mass range allows for new measurements at a higher precision than accepted values.

This work includes design, thorough extensive computer modeling studies, new ion cyclotron resonance accelerator cells, improved beam optics and detection electronics, and a sophisticated data system. With the resulting improvements in magnetic and electric fields, improved cell design, more capable and integrated analysis tools, and an enhanced data system, we anticipate reaching the desired precision of one part in 10^9 over a mass range of 16 u to 250 u.

Computer modeling of the ion cyclotron resonance system is a crucial aspect of this work, in order to understand the physics of the system, and to realize the most sensitive parameters to modify for improved performance. Such modeling includes magnetic and electric field calculations in three dimensions to determine the high order terms in these fields. This information is fed into ion motion simulations to study the detailed impact of non-uniformities on trapping, excitation, and detection. Such modeling will have a significant impact on improving the performance of FTICR-MS for all applications. We have previously carried out a number of studies of these ion cyclotron resonance devices using computer models of the ion motion in order to look at the effects of magnetic field inhomogeneities and non-ideal electric fields on the ion motion, using Monte Carlo techniques and integration of the particle motion.

The dynamical system that lies at the heart of any successfully operating ion cyclotron resonance mass spectrometer is a charge cloud which is trapped by a combination of electrostatic and magnetic forces. Several non-neutral plasma groups have also studied this system both theoretically and experimentally for the past 20 years. There is little doubt that a closer link between these two communities would be of benefit to both. Several such applications are immediately apparent. For example, plasma physicists have worried extensively about the importance of azimuthal symmetry in the dynamics of a charge cloud. Since ion cyclotron resonance cells come in both cubical and cylindrical geometries, azimuthal symmetry or the lack thereof has implications for ion cyclotron resonance cell design. In addition, the long-term coherence of a large amplitude cyclotron mode is due in part to established physical principles long known in the non-neutral plasma domain. Since long transients are obtained only from a coherent cyclotron mode, it is critical that these principles be applied to the ion cyclotron resonance case.

Technical Accomplishments

We have applied the tools and concepts of non-neutral plasma physics to the physical problem of FTICR mass spectrometry. In some cases this led to an improved understanding of the pre-existing "art" of accurate mass measurement. In other cases, this work has given guidance as to how to redesign these instruments for more reliable and accurate operation. Modeling work was performed to understand the dynamics of cyclotroning charge clouds. The first phase of this work was to analyze the dynamics of particles within a single cloud. Subsequently, we analyzed the behavior of a number of interacting clouds each arising from a substance with a different mass. As a special case of this multi-cloud study, we analyzed the ability of FTICR to accurately measure the masses of nearly identical mass pairs at the same time.

During FY 1994, we concentrated on developing a solid theoretical understanding of the FTICR-MS process, through theoretical and computational simulations. A number of important space charge related effects which affect the performance of FTICR-MS were studied and publications submitted. This included a description of the stability of ion clouds, which had previously not been put upon a theoretical base.

The resolution, and thus the mass accuracy, of a FTICR-MS instrument is limited by the time that a transient is observed. Once an ion cyclotron resonance vacuum has been brought to the nanotorr level, and electric and magnetic field inhomogeneities have been controlled, the observation time is limited by the computer data acquisition system and electronics. Development has been carried out to provide very large (10 megaword) transients acquired at 10 MHz rates. Improvements in the electronics, including preamplifiers and digitizers, are necessary. Noise is the limit to obtaining single ion sensitivity, a goal for state-of-the-art instruments. We are assembling an improved FTICR-MS data system, based on a Summing Transient Recorder being built for us commercially with very large memory.

Publications

A. J. Peurrung and R. T. Kouzes. 1994. "Analysis of Space-Charge Effects in Cyclotron Resonance Mass Spectrometry as Coupled Gyrator Phenomena." *Int. J. Mass Spect.* (submitted).

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Presentations

A. J. Peurrung. 1994. "Coupled Gyrators." Presented at the 13th International Conference on Mass Spectrometry, Budapest, August.

A. J. Peurrung. 1994. "Multiple-Charge Cloud Effects in ICR-MS." Presented at the Non-Neutral Plasma Conference, Berkeley, California, July.

Other Accomplishments

A. J. Peurrung, the postdoctoral fellow who carried out this work this year, became a PNL staff member.

Michael Gorshkov, a well-known FTICR-MS researcher, was brought in to continue this work.

Functional Characterization of Bacterial Plasmids

James K. Fredrickson and Margaret F. Romine (Earth and Environmental Sciences)

Project Description

The principal objective of this project is to investigate the genetics of microbial biodegradative pathways to provide basic information necessary for the design and implementation of environmental and industrial processes based on microbial metabolism. The observation that numerous metabolic functions, such as metabolism of aromatic compounds, uptake of metals, metal resistance, and antibiotic resistance are encoded on large plasmids in other microorganisms, suggests that plasmids found in subsurface microorganisms might also carry similar characteristics. To date there has been little concerted effort toward genomic characterization of large bacterial plasmids, particularly those that encode for important genes involved in the biodegradation of organic contaminants.

This research will identify metabolic functions associated with large plasmids in the subsurface bacterium F199 and closely related strains isolated from deep subsurface sediments of the Atlantic Coastal Plain, tentatively identified as belonging to the genus *Sphingomonas*. The technical focus is on determining if aromatic catabolism genes are encoded on these large plasmids. Multiple approaches will be used to accomplish this including chemical and transposon mutagenesis and DNA:DNA hybridization.

Technical Accomplishments

During FY 1994, we investigated the biodegradative capabilities of six different subsurface and two ATCC bacteria belonging to the bacterial genus *Sphingomonas*. The subsurface bacteria included Subsurface Microbial Culture Collection (SMCC) (Florida State University) strains F199, B0477, B0478, B0522, B0695, and B0712 and, for comparison, American Type Culture Collection (ATCC) strains 14666 (*S. capsulata*) and 29837 (*S. paucimobilis*). The ability to grow on naphthalene, toluene, *p*-cresol, *o*-xylene, *m*-xylene, *p*-xylene, dibenzothiophene, fluorene, biphenyl, benzoate, and salicylate as sole carbon sources was determined for each of these strains (see the table). Neither of the ATCC strains nor B0477 was able to grow on any of these compounds. All of the other subsurface strains were able to grow on naphthalene, toluene, all isomers of xylene, and salicylate. Strains B0478 and B0712 were unable to grow on *p*-cresol while only B0478 was unable to grow on benzoate. In addition, all of the subsurface strains except for B0477 were able to degrade dibenzothiophene, fluorene, and biphenyl. These results demonstrate that multiple strains of the genus *Sphingomonas* in the SMCC have novel metabolic capabilities with regard to the range of aromatic contaminants they can metabolize. Hence, the hypothesis was developed that these strains harbored the genes for degradation of naphthalene and the methyl aromatics on extrachromosomal DNA elements called plasmids.

Each of these strains was then examined for presence of plasmids. We found that all strains had large plasmids (>100 kb) except ATCC 29837. Each of these strains contained two plasmid bands (either unique plasmids or different forms of a single plasmid) except for strains B0522 and ATCC 14666, which had one each. Several approaches were used to evaluate the hypothesis that the genes coding for the novel catabolic functions were encoded on these plasmids including plasmid curing, plasmid transfer, and mutagenesis.

To generate mutants in the *Sphingomonas* biodegradative genes, a system was optimized for transfer of a transposon onto host DNA. The transposon chosen was a modified Tn*5* carrying a promoterless *gus* gene at one end and the tetracycline and kanamycin resistance genes. The promoterless *gus* gene would allow future work on screening for *Sphingomonas* promoters. The construct, pRK600, is unable to replicate outside the *E. coli* host and is lost upon transfer. The loss of the plasmid after transfer can be confirmed by loss of the vector-encoded chloramphenicol resistance gene. Transposition of Tn*5* into the genome is then selected for by acquisition of tetracyline and kanamycin resistance in the host.

Initial attempts at curing, transferring, or mutating plasmid(s) in F199 were unsuccessful using lack of growth of putative mutants as an assay. The lack of success was because growth is an ineffective assay for screening for such mutants. Alternative assays to test for the inactivation of the biodegradative functions were developed. Many of the metabolites produced during the degradation of aromatic compounds are highly colored and easily detected in agar of broth media. Therefore, colored intermediates that would likely be produced during microbial metabolism of select compounds is an alternative assay. Colored products generated from growth on these compounds diffuse out from colonies on the media in the immediate area of the colony that is able to degrade the compound. The production of colored metabolites is often accompanied by a zone of clearing around the individual colonies indicating degradation of the parent compound.

Various cosmid clones of pNL1, the plasmid in strain F199 hypothesized to harbor aromatic catabolic genes of the F199 plasmid, were obtained for expression of biodegradative activity in *E. coli*. We found that a number of these cosmids encoded catechol 2,3 dioxygenase (C23O) enzyme activity. The enzyme catalyzing this activity is a common intermediate found in each of the known pathways for degradation of the compounds listed in the table. These results demonstrate that aromatic catabolic activities are encoded on pNL1 and provide strong evidence that the hypothesis is true. C23O activity was mapped to a large *notI* fragment of pNL1, approximately 45.5 kb in size. There is evidence that a second C23O enzyme is also harbored on pNL1. Preliminary DNA sequencing from cosmid clone 18 identified a region of DNA that is highly homologous to C23O sequences found in the GENBANK database. Primers designed from these sequences did not hybridize to a second cosmid clone, designated clone 6, which also expressed catechol degradative activity in *E. coli*. The lack of any overlapping regions with clone 18, suggests that a second C23O enzyme resides on this clone and not on clone 18. Each of the catechol degrading clones was also able to degrade 4-methyl catechol.

Because biodegradative pathways are often found together on an operon, cosmids 4, 6, and 18 were tested for ability to grow on naphthalene, dibenzothiophene, fluorene, biphenyl, and toluene as the sole source of carbon and energy. No growth was observed on any of these compounds. These results suggest that 1) none of the genes necessary for these degradative activities reside in the region of pNL1, 2) these cosmids contain only part of the pathways necessary for growth on these compounds, 3) the genes are not expressed in the *E. coli* host, or 4) the genes are elsewhere on the pNL1 plasmid.

To test the possibility that degradative genes in addition to C23O are encoded on pNL1, but expressed at levels below detection, a system was optimized to transfer cosmid DNA into *Sphingomonas* strain ATCC 29837, which contains no native plasmids and is unable to degrade any of the aromatic compounds. An 8.5 kb broad host range cosmid vector, pUFRO42, was chosen as the transfer vehicle. It encodes genes for gentamycin and neomycin/kanamycin resistance. Strain 29837 is sensitive to kanamycin allowing us to select for uptake of this cosmid. The mating partner, HB101, and not 29837 was found to be sensitive to polymyxin B allowing for selection against the donor strain in a mating experiment.

In summary, the major technical accomplishments made by this project during this year include:

- Analysis of SMCC *Sphingomonas* strains for novel metabolic capabilities and the presence of plasmids.
- Development and optimization of rapid assays for screening mutants and clones for the ability (or lack thereof) to degrade the various aromatics.
- The development of mating systems and vectors that can be used for transposon mutagenesis and expression of cloned DNA in *Sphingomonas*.
- Confirmation that genes for aromatic catabolism (C23O) are encoded on pNL1, the large plasmid harbored by subsurface *Sphingomonas* strain F199.

Ability of Bacterial Strains to Grow on or Degrade Aromatic-Based Contaminants

Bacterium	Naphthelene	Toluene	*p*-cresol	*o*-xylene	*m*-xylene	*p*-xylene	DBT	Fluorene	Biphenyl	Benzoate	Salicylate
14666	-	-	-	-	-	-	-	-	-	-	-
29837	-	-	-	-	-	-	-	-	-	-	-
B0477	-	-	-	-	-	-	-	-	-	-	-
B0478	+	+	-	+	+	+	+	+	+	-	+
B0522	+	+	+	+	+	+	+	+	+	+	+
B0695	+	+	+	+	+	+	+	+	+	+	+
B0712	+	+	-	+	+	+	+	+	+	+	+
F199	+	+	+	+	+	+	+	+	+	+	+

Publication

J. K. Fredrickson, D. L. Balkwill, G. R. Drake, M. F. Romine, D. B. Ringelberg, and D. C. White. 1995. "Aromatic-Degrading *Sphingomonas* Isolates from the Deep Subsurface." *Appl. Environ. Microbiol* (submitted).

Presentations

M. F. Romine, J. K. Fredrickson, J. Saffer, L. Stillwell, and R. Schneider. 1994. "Biodegradation of aromatic compounds by *Sphingomonas* subsurface isolates." Presented at the Annual Meeting of the Society for Industrial Microbiology, Boston, Massachusetts.

L. Stillwell, R. Schneider, J. Fredrickson, M. Romine, and J. Saffer. 1994. "Isolation and Characterization of a 140 kb Plasmid from Subsurface Bacterium F199." Presented at the 1994 Annual Meeting of the American Society for Microbiology, Las Vegas, Nevada.

Other Accomplishments

Dr. Margaret Romine (Ph.D. in Microbial Genetics) was hired as a scientist in the Environmental Microbiology Group at PNL.

Graphical Interface for Ocean Global Circulation Models

Donald W. Denbo (Marine Sciences Laboratory)

Project Description

The goal of this project was to design and prototype a single, consistent graphical user interface to simplify the use of several ocean general circulation models (OGCMs).

The design of a single, consistent graphical user interface for several OGCMs was accomplished by first setting design constraints and goals. The design was constrained to only manage ASCII files that are used as input to OGCMs and to use only ASCII files for log, configuration, and temporary files. These constraints were chosen to simplify the design and to guarantee that all files handled by the program would be human readable. The design goals require that the interface be extensible (additional fields should be easily added to the interface), flexible (input for several different OGCMs should be easily managed by the program), and usable (the interface should be easier to use than managing the input files by hand).

Technical Accomplishments

The design chosen to meet the above constraints and goals is shown in Figure 1 - File Management System (FMS). The file management system uses a system configuration file to inform the system of the number of files and their names. Three files are used by the file management system to describe each managed file: 1) the configuration files that contain the parameter definitions, 2) the template file, and 3) the help file. A session file is used to provide continuity between sessions. The session file contains all the information required to recreate the state of the file management system.

A prototype of the design was created using a tool that produces graphical interfaces following the Motif style guidelines. The main window is shown in Figure 2. The prototype was developed using the requirements of the Parallel Ocean Program being developed at Los Alamos National Laboratory and then demonstrated.

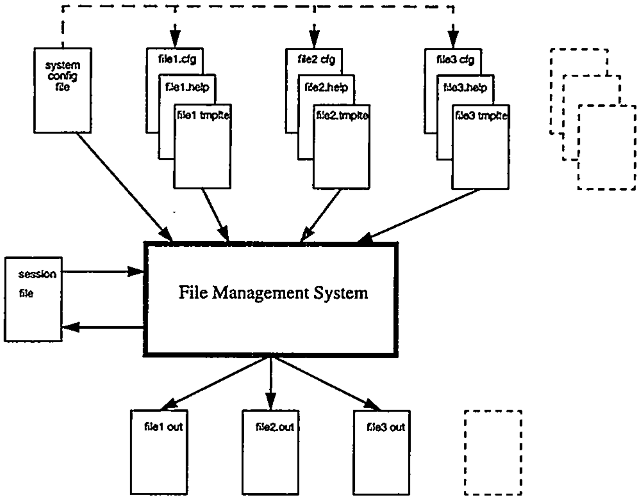
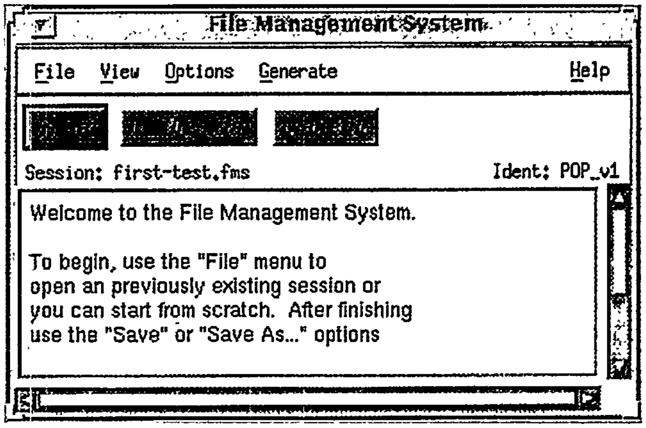


Figure 1. Functional Elements of the File Management System



Session: first-test.fms

Ident: POP_v1

Welcome to the File Management System.

To begin, use the "File" menu to open an previously existing session or you can start from scratch. After finishing use the "Save" or "Save As..." options

Figure 2. File Management System Main Window

Health Protection and Standards for Hazardous Chemicals

Barbara L. Harper (Health Risk Assessment)

Project Description

This project evaluated the toxicological basis of existing regulatory standards for many radionuclide and chemical contaminants. As an area of special emphasis, it also reviewed the supporting evidence used for the development of dose- and risk-based regulatory standards for several chlorinated solvents. In the laboratory, mechanisms of toxicity are being studied for chlorinated solvents, which are important for understanding and potentially changing the regulatory basis for setting exposure and cleanup standards. Sensitive methods for detecting DNA damage due to malondialdehyde and oxidative stress (two possible sources of DNA damage and ultimately carcinogenicity from carbon tetrachloride) are being developed to determine which is better correlated with tumor development. A better understanding of the relative roles of cytotoxicity and mitogenicity (excessive cell division) in tumor development will influence the derivation of regulatory standards and will improve their precision.

Technical Accomplishments

Initial toxicology profiles were developed that identified the reference doses and cancer slope factors for selected chemicals and radionuclides and presented supporting evidence for each. These profiles are intended as a quick reference for performing site risk assessments. Internal and external peer review was conducted.

A manuscript was prepared that discusses risk assessment issues specific to Native Americans, who are major stakeholders at Hanford. Their concerns go beyond the conventional approach to risk assessment, and include much more than unique exposure parameters. In order to evaluate impacts of site activities on Native American "health," one must also evaluate environmental and sociocultural impacts within the risk assessment framework, and incorporate quantitative indicators of impact, equity, and sustainability for each area. Just as important, one must integrate the results in the three areas over space and time, over multiple generations, and for key resources and cultural activities. The methodology for implementing this holistic approach to risk assessment and impact analysis is under development. The manuscript is undergoing peer review and will be submitted for publication.

An in-depth review of five chlorinated solvents (chloroform, dichloromethane, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene) has been prepared and will be published as a PNL report. These solvents have similar chemical properties but distinct biological activities and toxicities. For each solvent, toxicity, regulatory basis, and data limitations were identified and discussed. In addition, new knowledge about the mechanism(s) of toxicity, especially related to molecular mechanisms of carcinogenicity, will support an expanded and integrated LDRD research program in FY 1995.

Laboratory research efforts began this year to evaluate different types of toxicity that lead to cell damage and/or carcinogenicity. Results of this work will form the basis for suggesting changes in the way that toxicity information is used to derive regulatory standards used in risk assessments. Risk estimates for carcinogenic halogenated organic solvents are dependent on whether one assumes that the solvent causes tumor development through a genotoxic (direct DNA damage) or nongenotoxic mechanism. If evidence for genotoxicity exists, then the tumor data is extrapolated using the linear multistage model to estimate the upper 95% confidence limit of the dose that causes a one-in-a-million excess cancer risk; this is a very conservative method. On the other hand, if evidence of genotoxicity is lacking, other types of models (generally nonlinear) are used and risk estimates are less conservative. Thus, the model selected for risk estimates will have a major impact on the amount of effort required for cleanup of waste sites, and particularly on cleanup costs.

Even though exposure of laboratory animals to carbon tetrachloride and certain other halogenated solvents results in tumors, neither the parent compounds nor their metabolites bind covalently to DNA. This suggests that the carcinogenicity of these compounds arises from a nongenotoxic mechanism. Two pathways, both leading to DNA damage, have been proposed. First, reactive oxygen species including the hydroxyl radical are produced as byproducts of cytochrome P450-catalyzed reactions; this leads to oxidative DNA damage in several forms including the production of 8-hydroxydeoxyguanosine and thymine glycol. Second, carbon tetrachloride is metabolically converted to radical species which produce lipid peroxidation products that decompose to several compounds including malondialdehyde. Malondialdehyde is thus a product of lipid peroxidation rather than a direct metabolite of carbon tetrachloride. Malondialdehyde can react with deoxyguanosine of DNA to form covalently bound adducts, which are known to be mutagenic (the presumptive initiating step in the carcinogenic process).

Because of the efficient biological defense mechanisms for quenching radicals and repairing damage to DNA produced by these indirect means, it is probable that the dose-response relationships at low doses are not linear.

Thus, it becomes important to determine the dose-response relationships involved with such mechanisms relative to the cytotoxic effects of carbon tetrachloride known to occur in the livers of humans and experimental animals. These data should provide the theoretical and quantitative basis for developing alternative cancer risk assessment models for carbon tetrachloride.

High Field NMR and NMR Imaging

Gary P. Drobny (University of Washington)

Project Description

The objective of this project is to apply high resolution nuclear magnetic resonance techniques to the study of synthetic DNA oligomers displaying lesions generated by ionizing radiation and DNA oligomers displaying interstrand cross links resulting from interactions with various drugs, toxins, and toxicants. Initial work concentrated on the preparation of a DNA octamer with 5,6-dihydrothymidine substituted at a single thymidine site. More recent work performed in collaboration with Paul Hopkins at the University of Washington has resulted in the preparation of small amounts of DNA oligomers with cross links resulting from exposure to mitomycin C, cisplatin, and nitrous acid. Nuclear magnetic resonance structural studies of DNA with interstrand cross links are important for understanding the molecular level impact of these drugs and toxins. In addition to studies of chemically altered DNAs, a structural study of a series of surface charge mutants of the B1 domain of protein has been initiated. This study is part of an effort to elucidate at atomic level resolution, the mechanism whereby acidic proteins affect the nucleation rates of various biological composites.

A systematic study by high resolution nuclear magnetic resonance of the three-dimensional structures of the DNA sequences preferred by various cross-linking agents and the three-dimensional structures of the cross-linked DNAs has never been undertaken. The objective of this LDRD project is to initiate such a study. We feel this nuclear magnetic resonance study will provide structural information necessary to understanding the conformations of DNA that are involved in cross-linking and the reaction of the double helix to the significant perturbations induced by these cross links. Furthermore, the collaboration with the Hopkins group makes possible the investigation of the chemistry and structural impact of a broad family of cross-linking agents, in contrast to a more conventional and exhaustive study of a single lesion.

Technical Accomplishments

The most significant progress made during the recent year is the preparation of a DNA octamer with a single 5,6-dihydrothymidine lesion substituted into the sequence as well as the preparation of a series of DNA oligomers with interstrand cross links. The former work is a collaboration with a research group currently using high resolution nuclear magnetic resonance to study the structural and dynamical impact of this lesion. The latter work is a collaboration with a research group at the University of Washington. The formation of in vivo cross links following exposure to bifunctional electrophiles such as cisplatin and nitrogen mustard has been established as the basis for the extreme toxicity of these substances. Interstrand cross-linking in DNA is also considered to be the basis for the cytotoxic activity of many antitumor drugs. It is also known that small molecules of the type considered in this study display strong sequence preferences.

Our progress in 1994 has been mainly in the area of sample preparation. Cross-linked DNAs have rarely been prepared in amounts sufficient for high resolution nuclear magnetic resonance study. During the 1994 spring and summer quarters, DNA oligomers containing a cross link from reaction with a so-called Fujisawa cross-linking agent were prepared in amounts sufficient for high resolution nuclear magnetic resonance study. Fujisawa cross-linking agents are similar to the mitomycins. Although a mitomycin cross-linked DNA has been studied by others, the distance constraints on that structure are so wide as to make the study of questionable value. Now that we can prepare DNA oligomers with Fujisawa cross-links in nuclear magnetic resonance quantities, we are in a position to initiate an nuclear magnetic resonance study of the structural impact of the cross link.

Our main objectives and accomplishments, however, have been to prepare near-nuclear magnetic resonance quantities of DNA oligomers cross-linked with nitrous acid and cisplatin. Nitrous acid HONO is the conjugate acid of sodium nitrite. Hopkins' work has shown that this agent selectively cross-links 5'-d(CG) and the lesion is essentially a bridge between the exocyclic nitrogens of dG. As a result of our recent efforts, DNAs containing this lesion can be prepared in circa 0.5 mM concentrations (0.4 mL volumes). Such concentrations are usable if we get access to the 750 MHz nuclear magnetic resonance spectrometer at PNL.

Because HONO cross-links exocyclic nitrogens in dG, its point of attack is the minor groove. We have also made efforts to prepare nuclear magnetic resonance quantities of cisplatin cross-linked DNAs. As a result of work conducted in collaboration with Hopkins in 1994, nuclear magnetic resonance quantities of the cisplatin lesion are also available. Cisplatin is a reasonable complement to the HONO study because cisplatin's point of attack is the major groove. Hopkins has shown that 5'-d(CG) is cross-linked dG-to-dG and a cross-linking of N7 to N7 is the most reasonable hypothesis. As a result of our efforts in 1994, we can initiate a nuclear magnetic resonance study of cisplatin cross-linked DNA as well.

There were some disappointments in sample preparation however. Formaldehyde is a ubiquitous chemical pollutant and a known cross-linking agent. Formaldehyde cross links are known to bridge N6 of dA on opposite strands. The formaldehyde cross-linked DNAs prepared recently are too labile for nuclear magnetic resonance study. Other cross links are labile to some degree, and a feature of this entire project which makes access to PNL's high field facility a necessity is that cross-linked DNAs show progressive deamination. Nuclear magnetic resonance studies of even cisplatin and HONO cross-linked DNA samples must be concluded within 48 to 72 hours.

Protein nuclear magnetic resonance studies have also advanced during 1994. *Cro* protein has been purified and nuclear magnetic resonance studies are being conducted in collaboration with Mike Kennedy. The B1 domain of Protein G has been expressed and labeled with both 15N and 13C. Two-dimensional and three-dimensional studies of Protein G's B1 domain are in progress (see the HCCH TOCSY and HNCACO spectra). Formation of numerous biological composites is controlled by acidic proteins and with eleven aspartic acid and glutamic acid residues, Protein G is a useful model system for probing composite-protein interactions. In fact, work by Pat Stayton (Department of Bioengineering, University of Washington) and Allison Campbell (PNL) indicates that Protein G induces nucleation of calcium oxalate while surface charge mutants of Protein G actually inhibit nucleation. We intend to use high resolution nuclear magnetic resonance to determine the structure of a series of surface charge mutants of Protein G, prior to initiating study of composite-protein interactions by solid-state nuclear magnetic resonance.

Publication

L. Zhu, B. R. Reid, M. A. Kennedy, and G. P. Drobny. 1994. "Modulation of J-couplings by cross relaxation in DNA sugars." *J. Magn. Reson.* Series B (in press).

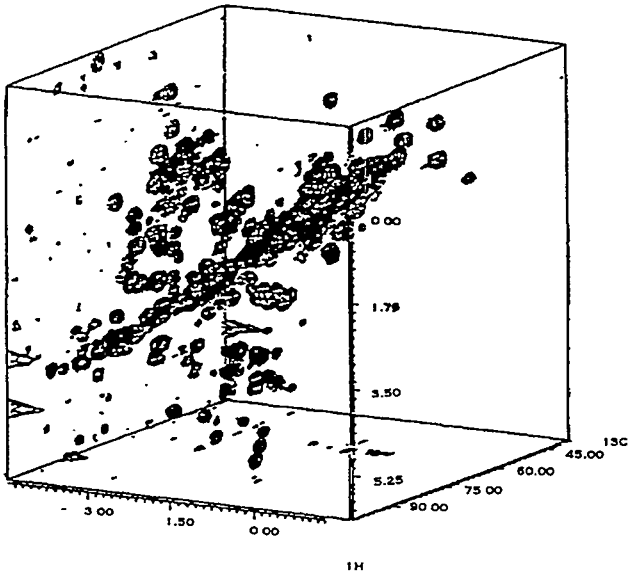


Figure 1. Portion of the HCCH TOCSY Spectrum of ^{13}C-Labeled Protein G (B1 Domain)

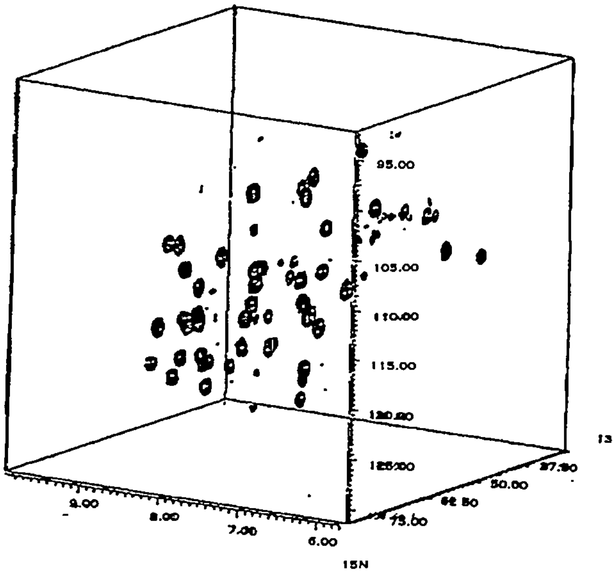


Figure 2. HNCACO Spectrum of Doubly Labeled Protein G

Human Metabolic Parameter Development for PBPK-Based Breath Analyzer Model

Robert D. Stenner, Brian D. Thrall, and David L. Springer (Biology and Chemistry)

Project Description

The objective of this project was to establish a laboratory for determining unique physiologically based pharmacokinetic (PBPK) model parameters. The effort focused on developing a capability to determine unique parameters, such as human metabolism rates where ratioing of in vitro versus in vivo animals results are used to derive in vivo human results from human in vitro data.

PBPK models are only as good as the experimental data used in their development. The development of a PBPK model requires an understanding of the mechanisms by which the chemical of interest is taken up, distributed, metabolized, stored, and cleared by the body. This project established an experimental method to develop pertinent human metabolic rate parameters for carbon tetrachloride (CCl_4), the chemical chosen to demonstrate the breath-analyzer system capability.

Technical Accomplishments

Laboratory space in the 331 Building designated for use in determining unique biokinetic modeling parameters was obtained. The facility included an existing gas chromatograph, gas chromatograph expendable supplies, and DB-Wax fused silica capillary columns for use in the CCl_4 metabolic parameter study. Work on the CCl_4 human metabolic parameter study began in early summer.

Analytical procedures were established for measuring the CCl_4, and preliminary runs were made on the gas chromatograph to establish and test the analytical capability. A preliminary study design was developed to begin the in vivo and in vitro animal studies to determine the ratios for the metabolic rate parameters.

Collaborative effort discussions with Washington State University were started on how the animal and human tissue slices were to be obtained and used. At this point, we were informed that funding would not be available to continue the CCl_4 human metabolic parameter study next fiscal year. As a result, work on CCl_4 human metabolic parameter development was stopped.

Other Accomplishments

The PC-based software, Advanced Continuous Simulation Language (ACSL) with Graphic Modeler, was obtained to aid in the development of PBPK models. The software enhances the laboratory capability by allowing segments of a PBPK model to be developed early on that can be utilized to examine behavior of the biokinetic parameters being studied. Early modeling of the parameters, using preliminary data or estimates, can significantly enhance study design.

Identification and Structural Determination of Paramagnetic Species Using Pulsed EPR

Michael K. Bowman (Macromolecular Structure and Dynamics)

Project Description

The objective of this project was to develop and demonstrate new Fourier transform electron paramagnetic resonance (EPR) techniques for the identification of free radicals and paramagnetic metal ions and for the determination of the local structure of their immediate surroundings. The techniques would be targeted to enzyme and free radical systems of major biological or environmental interest in order to be able to characterize structure and function in at least a local region for non-crystalline, impure samples.

Technical Accomplishments

Key intermediates in many important biological and chemical reactions are free radicals or involve paramagnetic metal ions. Because these intermediates are usually present in very small amounts, it is necessary to use sensitive and highly specific methods to identify and study them. In the case of free radicals and paramagnetic species, the method of choice is modern electron paramagnetic resonance spectroscopy, which can in many cases both identify and provide information about the electronic and physical structure of the intermediate. As useful as the existing electron paramagnetic resonance methods are, there is still much need for improvement, particularly for their application to paramagnetic species in enzymes and on catalytic surfaces where the concentration is of necessity limited. To this end, this project attempts to develop new methodologies for the investigation of these important species applicable to samples of environmental importance.

Important progress has been made in three new methods for extracting structural information about the surroundings of paramagnetic ions in proteins and complexes. These are nuclear cross-correlation peaks in HYSCORE spectra, forbidden lines in HYSCORE spectra, and second-order shifts in combination lines of two- and four-pulse ESEEM spectra. Each of these methodologies provide new information about interactions of the paramagnetic species with nearby nuclei, giving either a measure of the physical distance between them or the extent of electronic delocalization onto the ligand at the position of the observed nucleus. Each of these methods will be discussed in turn. Also, at the end of FY 1994, a Fourier transform electron paramagnetic resonance spectrometer with pulsed ENDOR capability was delivered to PNL. This will give us state-of-the-art experimental capabilities and will accelerate progress in this LDRD project by more tightly coupling theoretical and experimental work.

Nuclear cross-correlation peaks occur in HYSCORE spectra at positions that correlate the resonance frequency of one nucleus with that of another nucleus in the same paramagnetic species. We have succeeded in identifying those cross-correlation peaks in a VO^{+2}:histidine complex used as a model of a vanadyl probe of an enzyme metal binding site. We observed several cross-correlation peaks between the imidazole nitrogen of the histidine directly coordinated with the vanadyl and dipolar shifted protons from the solvent of the histidine. Because the sign of the coupling in these weakly shifted protons is known, the signs are therefore determined for the nitrogen hyperfine and quadrupole couplings. These can be related to the unpaired electron spin density at the nitrogen and to the sign of the electric field gradient at the nitrogen nucleus. This is important additional information for understanding the electronic structure of the metal-ligand complex.

We observed correlation peaks in some HYSCORE spectra that could not be interpreted on the basis of the established selection rules for such peaks. We have explained them as forbidden peaks that become observable under weak excitation conditions. An expansion of the pulse evolution operator clearly shows the formation of these peaks and allows quantitative predictions of their amplitudes which remain to be verified in FY 1995. These peaks should prove extremely important in the interpretation of HYSCORE spectra from unoriented samples of catalysts and metallo-enzymes. There are often accidental degeneracies in the nuclear frequencies that complicate interpretation of the spectra. These forbidden peaks contain additional information that will remove many of the ambiguities in the spectral interpretation when there are accidental degeneracies.

Finally, substantial progress has been made in the interpretation of the combination peaks in two- and four-pulse ESEEM spectra. These are generally very narrow, intense peaks because they are not broadened by hyperfine anisotropy to first order. However, there is a second order shift in the peak position caused by the anisotropic portion of the hyperfine interaction. These shifts have been observed and interpreted on proton peaks in a vanadyl probe bound to D-xylose isomerase. These shifted peaks are from protons on the histidine coordinating the vanadyl probe. From the size of these shifts and their orientation dependence, we were able to show that the histidine plane is nearly perpendicular to the equatorial plane of the vanadyl. The derived distance between the protons and the vanadyl from these measurements is consistent with this interpretation. These second-order shifted peaks are exciting because they should also appear along the diagonal in HYSCORE spectra and allow similar information to be obtained from those spectra.

Other Accomplishments

Dr. Sergei Dikanov, a senior member of the Institute of Chemical Kinetics and Combustion of the Siberian Branch of the Russian Academy of Science was supported as an AWU Faculty Fellow in FY 1994 and will be extended for an additional year. He is one of the world's leading experts in the interpretation of pulsed electron paramagnetic resonance spectroscopy and is making a major contribution to this LDRD project.

Professor Joanne Smieja from Gonzaga University has also joined the project for a year as an AWU Sabbatical Fellow. In FY 1995, we expect to have three experienced researchers joining the project for periods of 4 to 6 months through the SABIT program.

Improved Analytical Ion Trapping Methods

Steven A. Hofstadler, Michael G. Sherman, and Richard D. Smith (Chemical Sciences)

Project Description

This research is directed at ways to increase the utility and range of applications of ion trapping methods for analytical mass spectrometry for use in a broad range of applications. The research has emphasized use of computational and experimental studies to define improved trapped ion cell geometries for mass spectrometry, methods for more efficient trapping of externally generated ions, and the use of new electromagnetic field combinations to enhance performance. A new approach for large molecule, small particle, and possibly single cell characterization has been developed and is being explored for possible application to virus identification, the study of nanoparticle reactions, and potentially as a broadly useful method for "real-time" detection or characterization of larger submicron and micron size particles. At a broader level, the effort will provide an initial step toward a program aimed at implementing advanced mass spectrometric methods in support of DOE environmental, waste, remediation, and health effects research.

The need for improved analytical and characterization capabilities at DOE sites is enormous, including in situ tank characterization, groundwater monitoring, atmospheric sampling, in situ remediation support, bioremediation studies, broad laboratory-based analysis capabilities, the monitoring of waste processing, transport, and disposal, as well as health effects research. It has been demonstrated that improved analysis/characterization methods, and their increased utilization, can substantially decrease the cost of cleanup activities. However, current support in development of advanced methods is fragmented and primarily driven by near-term demands. The transfer and implementation of new technologies (developed at PNL and elsewhere) has been slow, with rate-limiting steps including the transfer of new technologies for commercialization and their subsequent adoption for application. As a result, investment in the development of advanced capabilities is limited, and unlikely to have a significant impact on DOE site cleanup. One aim of this project is to examine a new paradigm for this process with the intent of circumventing these difficulties and speeding the vertical integration of improved analytical instrumentation.

Technical Accomplishments

During the first year of this project, efforts determined appropriate conditions, based upon computer modeling studies, for effective trapping and measurement of individual particles. This provided the potential basis for a greatly improved analytical methodology for characterization of a broad range of "particles," spanning the spectrum from those of biological interest (i.e., individual cells, chromosomes, viruses, etc.) to those relevant to the development of new materials. As a demonstration of this approach we initially observed, over the course of numerous remeasurements, shifts to higher m/z for individual poly[ethylene glycol] (PEG) ions reacting with added neutrals (crown ethers) or residual background gas constituents. We also observed multiple reaction steps for single ion charge transfer during the transient decay from a single time-domain fourier transform ion cyclotron resonance (FTICR) transient. This stimulated the development of a novel approach for examining data referred to as "time resolved ion correlation" (TRIC). The TRIC technique was developed to more effectively examine the time dependence of individual ion signals and to establish a time-resolved link between reactant and product ion. The TRIC technique relies on the production of individual time-domain signals to follow reaction processes for each ion observed. Comparison of several individual ion time-domain signals extracted from a single transient generally allows a correlation between the appearance and disappearance of individual ions to be constructed. This is possible even when numerous ions are simultaneously present due to differences in m/z (since large ion transitions are generally restricted to a relatively small m/z region of the spectrum) and the temporal signature provided by the TRIC analysis.

Figure 1 shows a mass spectrum transformed from a 60-second transient, decay from a single poly[ethylene

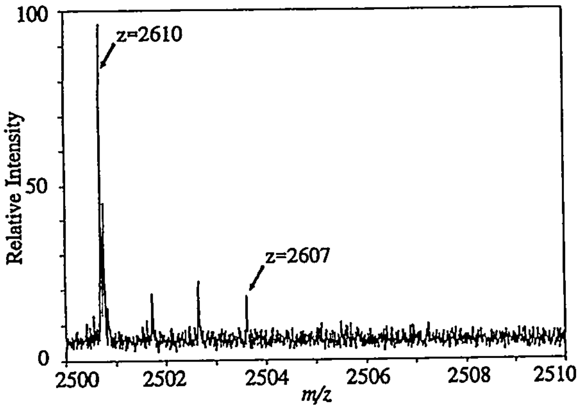


Figure 1. ESI-FTICR Mass Spectrum Transformed from a 60-Second Transient Decay from a Single Poly[ethylene glycol] Ion Isolated in the Trap

glycol] ion. By transforming discrete portions of the transient, it is apparent that each species is observed at different times during the transient and, most importantly, the disappearance of one species coincides exactly with the appearance of another species as demonstrated by the TRIC spectrum in Figure 2. The step-wise shifts shown in Figure 2 allow the charge to be determined, yielding an ion mass of 6.527 MDa. We can thus observe the step-wise reaction of the ion, and in separate experiments have been able to observe the reactions of individual trapped ions for periods in excess of several hours. Single ions of bovine albumin having as few as 30 charges have been detected with signal-to-noise levels of ≈2. Such measurements could also be substantially speeded by the ability to measure a number of individual ions simultaneously by observing the time resolved reaction steps in the course of a single transient.

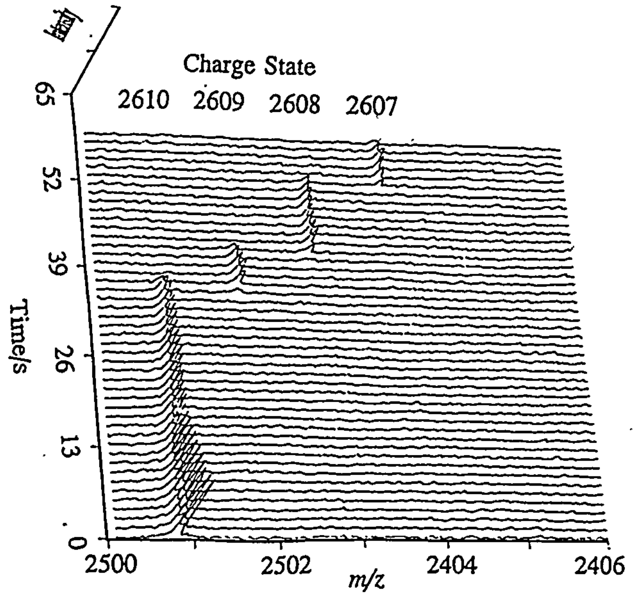


Figure 2. Time domain data for an individual ion in the FTICR trap showing three reaction steps during the observation period. The m/z shifts allow calculation of an accurate ion mass (of 6.527 MDa), and provide the basis for future studies aimed at probing structure, and the extension of the technique to much larger particles.

In an alternative, yet complementary scheme, we have employed a direct charge measurement method suitable for very large (> > 1 MDa) ions. Preliminary direct charge measurements obtained from individual ions from a (nominal) 1.1 x 10^8 Da Coliphage T4 DNA sample derived from *Escherichia coli* B host strain ATCC (American Type Culture Collection), are in the molecular weight range expected, indicating that the ions are substantially intact. The masses determined for the largest peaks were all determined to be in the range of ~100 MDa. These preliminary results show that even extremely large ions can be effectively transferred to the gas phase and be studied by the ESI-FTICR process.

The analysis of very large ions by FTICR affords unique opportunities to study fundamental interactions of charged particles in the trapped ion cell, as well as ion-molecule and ion-ion interactions. For example, under pressure limited conditions, the transient from a highly charged individual ion will be longer than from an ensemble of smaller ions since loss of phase coherence is not possible for an individual ion. Signal from Coliphage T4 DNA individual ions at a pressure of ≤1.0 x 10^{-9} torr has been detected >90 minutes after initial excitation. These results also suggest that the defacing effect (loss of coherency) is of greater importance than damping of cyclotron motion in signal decay of an ion cloud for larger molecules. Because larger ions produce such long-lived time-domain signals, their reactions with other species (background neutrals, reactive gases, etc.) can be closely monitored during a single transient by using the TRIC techniques. While the physical size of these ions is uncertain, the extensive charging (and relatively low m/z) suggests that they undergo Coulombic extension during the electrospray process, and may have lengths on the order of 100 μm! The large number of charges carried by each of these ions also creates a unique situation for the study of ion-ion interactions and Coulombic effects.

Other potential applications of individual ion analysis methods include the characterization of synthetic polymers, large structural proteins, and DNA restriction fragments, for which mass determinations should be at least 102 more precise than by electrophoresis. DNA sequencing may be possible if a method can be developed to induce the stepwise degradation of a trapped oligonucleotide ion. It should also be possible to investigate selective non-covalent associations of small molecules with large molecules in solution by trapping such complexes and inducing their dissociation in the FTICR cell. The upper MASS range is uncertain, but the initial electrospray droplet charging (~10^5) and the m/z range available by FTICR (>200,000) suggest molecules in excess of 10^9 Da may be amenable to study.

Publications

J. E. Bruce, X. Cheng, R. Bakhtiar, Q. Wu, S. A. Hofstadler, G. A. Anderson, and R. D. Smith. 1994. "Trapping, Detection, and Mass Measurement of Individual Ions in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer." *J. Amer. Chem. Soc.* 116, 7839-7847.

R. Chen, Q. Wu, D. W. Mitchell, S. A. Hofstadler, A. L. Rockwood, and R. D. Smith. "Direct Charge Number and Molecular Weight Determination of Large Individual Ions by Electrospray Ionization-Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." *Anal. Chem.* (in press).

S. A. Hofstadler, Q. Wu, J. E. Bruce, and R. D. Smith. "Enhanced Accumulated Trapping Efficiency Using an Auxiliary Trapping Electrode in an External Source Fourier Transform Ion Cyclotron Resonance Mass Spectrometer." *Int. J. Mass Spectrom. Ion Proc.* (in press).

D. W. Mitchell, A. L. Rockwood, R. Chen, and R. D. Smith. "Trapping Field-Induced Frequency Shifts for Orthorhombic and Cylindrical FT-ICR Ion Traps." *J. Chem. Phys.* (in press).

D. W. Mitchell, A. L. Rockwood, and R. D. Smith. "Frequency Shifts and Modulation Effects Due to Solenoidal Magnetic Field Inhomogeneities in Ion Cyclotron Mass Spectrometry." *Int. J. Mass Spec.* and *Ion Proc. (in press).*

R. D. Smith, X. Cheng, J. E. Bruce, S. A. Hofstadler, and G. A. Anderson. 1994. "Trapping, Detection and Reaction of Very Large Single Molecular Ions by Mass Spectrometry." *Nature* 369, 137-139.

Integrated Climate Change Analyses: A Pilot Study

Marilyn J. Quadrel (Environmental Management)
Stephan F. Rayner (Global Environmental Management)

Project Description

Global climate change research is funded at its current levels in large part because of the promise that it can produce information that will benefit decisions that address the long-term viability of our environment, economy, and social structure. However, there is typically little direct contact between scientists and those whom they would help. As a result, scientists find it difficult to shape their research in decision-relevant directions, extract pertinent results, format them in accessible terms, and ensure they have been understood. Decision makers also have difficulties in their efforts to identify the pertinent science, ask the right questions, and interpret and apply the answers they get. If not bridged, this non-trivial gap could waste the practical value of the research that is being produced and erode support for future research. This project will help to bridge the gap between scientists and decision makers. The 1994 pilot study proposed and tested decision analytic and organizational techniques to clarify the information that public and private decision makers need and to describe ways in which global climate change information can be most productively provided.

Scientific research is of little practical value if it does not address issues that matter to decision makers and reach them in a useful form. Failure to demonstrate practicality can threaten support for research programs whose budgets are justified by policy concerns, as is the U.S. Global Change Research Program (GCRP). Even in times of unlimited resources, it would not be enough to assume that the value of research is self-evident, or to make general claims about usefulness.

The research conducted in FY 1994 was a proof-of-principle study to develop, test, and recommend methods for assessing the context within which globally relevant policy issues are defined, decisions are identified, and choices are made. These methods would be applied by the GCRP at the front end of integrated assessment programs to better focus research efforts on topics that are likely to impact policy decisions and guide information exchange between the science and policy communities. The objective is to generate a "decision map" for a given policy issue that describes what decisions are on the policy agenda, who makes those, and how they are made. Ultimately, this information should suggest a research agenda for the GCRP, including where and how the GCRP might best inform key decisions.

The FY 1994 pilot study was interdisciplinary. Decision theory forms its conceptual core, providing a flexible, theoretically sound framework for identifying the decision variables to be addressed, eliciting and representing decision information, and integrating that information into both formal and descriptive analyses. Organizational theory prescribes the contextual variables to be accounted for in our decision analytic framework. And, environmental science provides a measuring stick for assessing the "fit" of these decisions and decision making information to what we understand about global climate change processes.

Technical Accomplishments

The FY 1994 pilot study produced four distinct products:

- An analytic framework that "braided" disciplinary perspectives and established the basis for identifying key decision makers and decisions relevant to global climate change mitigation and impacts.
- A protocol for eliciting decision information from representative decision makers.
- A worked example, based on 14 interviews, characterizing a sample policy issue, and a set of decisions that may be altered by appropriate climate change information if it were available.
- Preliminary assessments of the value of existing scientific information to these decision makers and recommendations for how integrated assessment priorities may be established, projects designed, and results packaged so that scientific information may be better incorporated into key societal decision processes.

In addition to these products, the research team made significant contributions to ongoing dialogue on this and related topics within the scientific community by participating in the National Forum on Environment and Natural Resources Research and Development; the National Academy of Sciences, Human Dimensions of Global Climate Change; and the National Academy of Sciences Review of U.S. Science and Technology.

Integrated Environmental Monitoring

Thomas J. Carlson (Earth and Environmental Sciences)

Project Description

The objective of this project was to develop a set of analytical procedures and software tools that can be used to improve monitoring network design decisions. Such decisions include the choice of monitoring locations, sampling frequencies, sensor technologies, and monitored constituents. Integrated environmental monitoring is being designed to provide a set of monitoring alternatives that balance the tradeoffs between competing monitoring objectives, such as the minimization of cost and the minimization of uncertainty. The alternatives provided are the best available with respect to the monitoring objectives, consistent with the physical and chemical characteristics of the site, and consistent with applicable regulatory requirements. The selection of the best monitoring alternative to implement is made by the decision maker after reviewing the alternatives and tradeoffs produced by this process.

Technical Accomplishments

During FY 1993, the framework for the network design process was conceptualized, development of a numerical test bed for the process was initiated, and approaches were developed to target user needs. During FY 1994, the framework was refined, a prototype tool set was assembled, a demonstration problem was defined with the help of potential customers, and work on the demonstration was initiated.

Refinement of a Decision Framework

A framework for monitoring decision making was developed during 1993. This framework was refined during 1994 to focus on critical tools for network planning. The refined framework is shown in the figure. The process began with identification of the monitoring objectives. The next step was to generate a set of monitoring alternatives that represent the tradeoffs that must be made between competing objectives. Several components are required to generate optimal monitoring network design alternatives. A conceptual model that represents the current understanding of the site ensures that the monitoring alternatives are consistent with the physical and chemical characteristics of the site. An uncertainty assessment quantifies what is unknown and uncertain about site characteristics. The conceptual model, the uncertainty analysis, and the objective statements are combined in a decision model that provides the actual mechanism for the generation of optimal monitoring alternatives. The decision model is a mathematical statement of the monitoring network decision process. The outcome of the design process is a tradeoff diagram that will allow decision makers to choose between monitoring alternatives in a more quantitative way than is currently available.

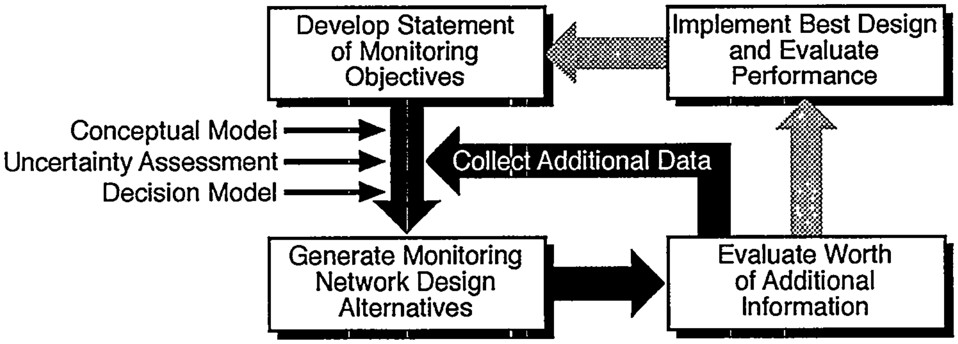
Prototype Tools Set

Existing tools were selected for use in demonstrating the design process. Tools include a groundwater flow model, a contaminant transport model, a geostatistical evaluation package, and an optimization algorithm.

Demonstration Problem

A demonstration problem was chosen that

- has relevance and applicability to current Hanford monitoring needs



Monitoring Network Design Framework

- has good prospects of stakeholder (DOE, users, regulatory agencies, public) acceptance
- achieves results with the available resources.

Two processes were used to identify relevant monitoring issues for the Hanford Site and determine if the theme would have stakeholder acceptance. The first process was to interview technical staff and project managers involved in groundwater monitoring on the site. The second was to examine the regulatory environment in which the integrated environmental monitoring tool set may be applied. Hanford's regulatory environment includes requirements of the Tri-Party Agreement and its revisions, as well as Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) requirements. The problem includes a waste site located near a high-quality river. The waste site may leak contaminants and the monitoring objectives are to minimize monitoring cost, minimize the probability that contaminants will reach the river undetected, and maximize the advance warning of a leak should one occur.

Presentation

R. W. Bryce, P. D. Meyer, L. W. Vail, T. J. Carlson, D. D. Hostetler, P. L. Miller. 1994. "Integrated Environmental Monitoring - Prototype Demonstration." PNL-SA-24336. Presented at 6th National Technical Information Exchange Workshop. Kennewick, Washington.

Integrated Regional Climate Change

Steven J. Ghan (Atmospheric Processes)
Mark S. Wigmosta (Near Surface Hydrologic Processes)

Project Description

Estimates of the impact of global climate change on land surface hydrology require climate information on spatial scales far smaller than those explicitly resolved by global climate models of today and the foreseeable future. In this project, we plan to develop a physically based method for translating the coarse resolution predictions of global climate models (100 km resolution) to the finer scale resolution (1 km resolution or finer) required for impact assessment studies, develop a detailed surface hydrology model for mountain watersheds, and use the translation method to drive the surface hydrology model to assess the capability of simulating the impact of climate change on regional-scale water resources.

Technical Accomplishments

Integrated assessments of climate change must address the disparity between the spatial scales resolved by global climate models (at least 100 km) and the spatial scales required for climate impact assessment, which in mountainous terrain are 1 km or less. In this project, we developed an integrated physically-based modeling system that spans the wide range in scales required for assessment of climate impacts on one particularly vulnerable component of the climate system, namely surface hydrology.

The modeling system consists of one-way coupled physically based process models of the atmosphere and watershed hydrology. The atmospheric model consists of a regional circulation model with climate physics (clouds, radiation, and surface physics) and a novel parameterization that accounts for subgrid effects of topography on clouds and precipitation. The parameterization represents subgrid variations in surface elevation in terms of probability distributions of discrete elevation classes. Separate cloud, radiative, and surface processes are calculated for each elevation class. The simulated surface temperature, precipitation, and snow cover for each elevation class can then be distributed to different geographical locations according to the spatial distribution of surface elevation within each grid cell. This Regional Climate Model (PNL-RCM) can be driven by winds, temperature, and humidity either observed on its lateral boundaries or simulated by a global circulation model. Simulations with the subgrid parameterization demonstrate superior predictions of precipitation and snow cover, compared with predictions at much higher spatial resolution but without the subgrid scheme.

The watershed hydrology model, PNL-WATERSHED, provides an integrated representation of hydrology-vegetation dynamics at the topographic scale described by digital elevation data (nominally 90 m). It includes a two-layer canopy model for evapotranspiration, an energy-balance model for snow accumulation and melt, a two-layer rooting zone model, and a quasi three-dimensional saturated subsurface flow model. Digital elevation data are used to model topographic controls on incoming shortwave radiation, precipitation, air temperature, and downslope water movement. The evapotranspiration component treats the effects of changes in air temperature, rainfall, cloud cover, irradiance, soil water potential, vapor pressure deficit, and wind speed. The model can be driven either by observed meteorology (precipitation, temperature, humidity, irradiance, and winds) or by meteorology simulated by the PNL-RCM.

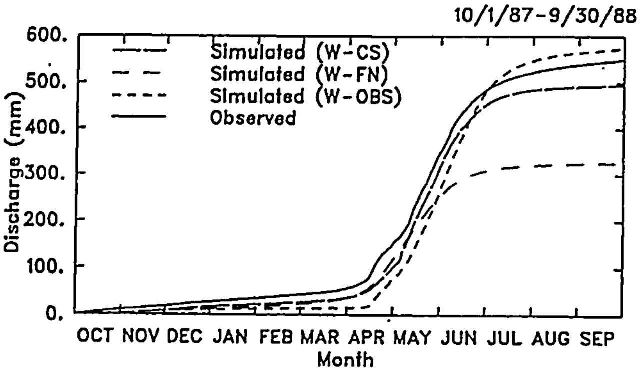
These two models were developed during the first 2 years of this LDRD project. A paper describing the performance of PNL-RCM in a 1-year Pacific Northwest simulation is in press. A paper describing the performance of PNL-WATERSHED in the Middle Fork Flathead River basin has been published. We have also produced a videotape illustrating the performance of PNL-WATERSHED, presented 13 papers at conferences, workshops, universities, and symposia, and prepared two proposals for external funding to continue this work.

In the remainder of this report we will focus on our recent progress in coupling PNL-RCM and PNL-WATERSHED. The coupling is one way, i.e., PNL-WATERSHED is driven by meteorology simulated by PNL-RCM, but does not influence the simulation by PNL-RCM (which has its own simplified treatment of surface hydrology).

Two coupled simulations have been performed. In the first, PNL-RCM is run at 90 km grid resolution, with its subgrid parameterization. In the second simulation the grid resolution is 30 km, but the subgrid parameterization is not implemented. In both simulations PNL-RCM is driven by lateral boundary conditions observed for the period October 1, 1987 - September 30, 1988. The

PNL-RCM domain spans 3200 km X 3200 km centered on the Pacific Northwest. PNL-WATERSHED is run for the Middle Fork Flathead River basin in western Montana, with meteorology from the PNL-RCM simulations. In addition, an uncoupled PNL-WATERSHED simulation is driven by meteorology observed at two stations within the Middle Fork Flathead River basin.

The figure compares time series of the simulated and observed accumulated discharge of the Middle Fork Flathead River for each simulation. The discharge simulated using meteorology from PNL-RCM with the subgrid parameterization is clearly superior to that without the subgrid parameterization, and is comparable if not superior to the discharge simulated using meteorology observed within the watershed. Note that results using simulated meteorology can be better than those using observed meteorology because only a few meteorology stations are available within the Middle Fork Flathead watershed, so that observed meteorology must be somehow distributed within the watershed. The process of distributing the precipitation and temperature introduces uncertainty that apparently is comparable to errors in the meteorology simulated by PNL-RCM.



Accumulated discharge of the Middle Fork Flathead River, as recorded (solid line), as simulated by PNL-WATERSHED driven by observed meteorology (short dashed line), as simulated by PNL-WATERSHED driven by PNL-RCM with the subgrid parameterization (long dashed line), and as simulated by PNL-WATERSHED driven by PNL-RCM without the subgrid parameterization (medium dashed line).

These and other results suggest that the integrated modeling system is nearly ready to be coupled with a Global Climate Model for climate change simulations.

Publications

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L. R. Leung, M. S. Wigmosta, S. J. Ghan, D. J. Epstein, and L. W. Vail. 1994. "Application of a Subgrid Orographic Precipitation/Surface Hydrology Scheme to a Mountain Watershed." *J. Geophys. Res.* (submitted).

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Integrated Systems Ecology as an Approach for Unifying Global Change Issues

Patricia M. Irving and Edward J. Rykiel (Earth and Environmental Sciences)

Project Description

Work in this project, was focused on innovative approaches to measuring, modeling, and predicting large-scale ecological change. This included developing the ability to assess the impacts and implications of local and regional landscape changes as a component of an integrated process-based earth system model.

This provided a means for addressing long-term problems in environmental management and restoration, as well as for coupling environmental knowledge and concerns with regulatory, economic, and policy decision needs.

Technical Accomplishments

Ecological Phase Transitions

The potential for using the concept of phase transitions to characterize ecological change was investigated. A variety of ecological phenomena at various spatio-temporal scales appeared to have the properties of a phase transition (e.g., the change from snow cover to bare tundra). As a first step in this development, we defined the terms of reference for ecological phase transitions and to cite empirical evidence of processes that conformed to these definitions. A presentation on the relevance of ecological phase transitions to global change was made at the First International Science Conference of the Global Change and Terrestrial Ecosystems (GCTE) Core Project of the International Geosphere-Biosphere Program. Another presentation citing ecological examples was made at the annual meeting of the Ecological Society of America. A draft manuscript is in preparation.

Arid Ecosystem Modeling

A logic for treating the intermountain sagebrush-steppe as a mosaic of distinct, hydrologically partitioned vegetation communities was developed and some critical ecophysiological considerations for process modeling of arid ecosystems was identified. The soil water and nutrient dynamics of a forest ecosystem process model (FOREST-BGC) were modified to simulate productivity and seasonal water use patterns in Artemisia, Agropyron, and Bromus communities on DOE's Fitzner/Eberhardt Arid Lands Ecology Reserve. Model relationships between soil water availability, transpiring leaf area, water use efficiency, and respiration costs of substantial below-ground productivity illustrate key ecophysiological considerations for arid land process modeling.

Ecological Models for Global Change

Literature on ecological models that might be useful for global change studies was collected and several of these models were examined in terms of the ability to link to GCMs, the usefulness for regional studies, and the usefulness for answering ecological prediction and management questions at the scale of human decision making. All the models examined lacked the components or scaling factors needed to answer any ecological questions on relevant space-time scales. Only one model, IMAGE (Integrated Model to Assess the Greenhouse Effect), included socioeconomic considerations and the Edmonds/Reilly energy model.

Integrated Regional Earth System Simulation Modeling

A variety of atmospheric, hydrologic, biogeochemical, and ecological process models have been constructed for use in global change studies. However, very little integration of these process models has been undertaken, in part because of the great differences in the space-time scales of the models. This research examined strategies for integrating atmospheric and hydrologic models developed at PNL with currently available ecosystem process models. A presentation of the conceptual model for linking atmospheric, hydrologic, and ecosystem components was made at the First International Science Conference of the Global Change and Terrestrial Ecosystems (GCTE) Core Project of the International Geosphere-Biosphere Program.

Publications

R. G. Kremer, E. R. Hunt, Jr., and S. W. Running. 1994. "Simulating vegetational and hydrologic responses to natural climatic variation and GCM-predicted climate change in a semi-arid ecosystem. *Journal of Arid Environments* (in review).

R. G. Kremer and S. W. Running. 1994. "Ecosystem process modeling in a semi-arid environment: coupling carbon and water dynamics to simulate seasonal patterns of resource utilization in contrasting vegetation communities." *Ecological Modeling* (in review).

E. J. Rykiel, Jr. 1994. "Ecological phase transitions and global change." In *First Global Change and Terrestrial Ecosystems Science Conference, Book of Abstracts*, Woods Hole, Massachusetts.

E. J. Rykiel, Jr., R. N. Kickert, and H. Wu. 1994. "Ecological Phase Transitions." *Bull. Ecol. Soc. Am.* Suppl. 75:201.

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M. S. Wigmosta, R. Leung, and E. Rykiel. 1994. "Regional modelling of climate-terrestrial ecosystem interactions." In *First Global Change and Terrestrial Ecosystems Science Conference, Book of Abstracts*, Woods Hole, Massachusetts.

Presentations

E. J. Rykiel, Jr. 1994. "Ecological phase transitions and global change." Presented at the First Global Change and Terrestrial Ecosystems Science Conference, Woods Hole, Massachusetts, 23-27 May.

E. J. Rykiel, Jr., R. N. Kickert, and H. Wu. 1994. "Ecological Phase Transitions." Presented at the Annual Meeting of the Ecological Society of America, Knoxville, Tennessee.

M. S. Wigmosta, R. Leung, and E. Rykiel. 1994. "Regional modelling of climate-terrestrial ecosystem interactions." Presented at the First Global Change and Terrestrial Ecosystems Science Conference, Woods Hole, Massachusetts, 23-27 May.

Other Accomplishments

A search was conducted for a senior research scientist to head integrated systems modeling from an ecological perspective. Dr. Edward J. Rykiel, Jr. of Texas A&M University was hired to fill this position and moved to PNL in July 1994.

Integration of Molecular Research with Environmental Phenomena

Raymond E. Wildung (Environmental Science Research)

Project Description

The objective of this project was to conduct research in organic geochemistry and microbial physiology and biochemistry through joint appointments at Washington State University (both in Pullman and at the Tri-Cities branch campus) that will link molecular-scale investigations in chemistry and microbiology to solutions of problems in environmental restoration.

There is a strong need to link capabilities being developed at the molecular level to resolution of problems being faced by DOE in environmental restoration. Key environmental processes that must be addressed include enzyme-level phenomena governing microbial biodegradation/sequestration and geochemical reactions occurring at mineral-solution interfaces. Together with hydrologic transport these phenomena govern contaminant mobility in the subsurface and form the basis for development of new remediation concepts.

Technical Accomplishments

Two new WSU/Tri-Cities positions have been established, which in conjunction with capabilities at PNL, serve as a basis for new research to define contaminant behavior and develop remediation measures based on an integrated understanding of biological and chemical phenomena.

In FY 1992, research was initiated on the degradation of synthetic chelates responsible for mobilization of metals and radionuclides in subsurface systems. Investigations were initiated to isolate and purify the enzymes responsible for nitrilotriacetate (NTA) degradation. In addition, a graduate student was recruited and funded to clone the genes regulating the expansion of these enzymes in subsurface microorganisms. In FY 1993, a NTA monooxygenase (NTA-Mo) was purified that has two protein components and the N-terminal amino acid sequence of one component was determined. A gene probe was designed using the N-terminal amino acid sequence and it was shown that the probe is specific to only one fragment of restriction-enzyme-digested DNA from Chelatobacter strain ATCC 29600. In addition, a summer student investigated the properties of NTA-Mo and found that the enzyme degraded nitrilotriacetate only when nitrilotriacetate was complexed with either Mg^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, or Fe^{2+}, but not with Ca^{2+}, Cu^{2+}, Cr^{2+}, Sn^{2+}, Ba^{2+}, Cd^{2+}, Sr^{2+}, Pd^{2+}, Al^{3+}, Cr^{3+}, K^{+}, Na^{+}. Several grant proposals were written and a National Science Foundation competitive research grant was awarded to investigate the biochemistry of 2,4,5-trichlorophenoxyacetate (2,4,5-T) biodegradation by *Pseudomonas cepacia* strain AC1100. An enzyme assay method was developed to detect 2,4,5-T monooxygenase and the enzyme purified. A postdoctoral fellow has been recruited to characterize the enzyme. Investigations were also initiated to characterize a water soluble blue pigment from a subsurface bacterium. The pigment properties suggest it is closely related to bacterial anthocyanins.

In FY 1994, the position in microbiology played a key role in developing advanced capabilities for use in bioremediation research. A tetrachloro-p-reductive dehalogenase was purified and labeled for nuclear magnetic resonance determination of structure. Initial nuclear magnetic resonance measurements have been conducted and appear feasible. The protein has been over expressed and new procedures developed for large-scale purification. The protein was also shown to be stable at room temperature for several weeks. With these accomplishments PNL is now poised to elucidate the structure using nuclear magnetic resonance. This will be the first application of the 750 MHz nuclear magnetic resonance spectrometer at PNL.

New studies are also delineating the mechanisms and key enzymes for 3-chlorobenzoate reductive dehalogenase in *Desulfomonile tijiei* and 2,4,5-T degradation by *Pseudomonas cepacia* AC1100. The dehalogenase enzyme has been purified although this involved surmounting major obstacles resulting from the slow growth of the organism and protein association with the cell membrane. The first enzyme involved in 2,4,5-T degradation has also been isolated and progress has been made on isolating the second enzyme involved in degradation. In addition, efforts were undertaken to clone and sequence the gene encoding monooxygenase. The monooxygenase was purified that was responsible for catalyzing the oxidation of nitrilotriacetate to iminodiacetate and glyoxylate and its N-terminal amino acid sequence determined. The responsible gene has been cloned using an oligonucleotide probe and partly sequenced.

Publications

D. E. Danganan, R. W. Ye, D. Daubaras, L. Xun, and A. M. Chakrabarty. 1994. "Nucleotide Sequence and Functional Analysis of the Genes Encoding 2,4,5-T Oxygenase in *Pseudomonas cepacia* Strain AC1100." *Appl. & Environ. Microbiology* (in press).

R. B. Reeder, L. Xun, A. E. Plymale, and H. Bolton, Jr. 1993. "Degradation of Several Metal-Nitrilotriacetate Complexes by a Partially-Purified Chelatobacter Monooxygenase." *Appl. & Environ. Microbiology* (submitted).

L. Xun, D. R. Boone, and R. A. Mah. 1994. "Preparation of Disaggregating Enzymes from *Methanosarcina Mazei.*" In: *Archaea-A Laboratory Manual.* Ed. R. T. Robb, Cold Spring Harbor Laboratory Press.

Interphase Chemistry

Donald R. Baer (Materials and Interfaces)

Project Description

The objective of this project was to develop new capabilities to examine, at the microscopic level, relationships between the structure of environmentally relevant liquid/liquid and liquid/solid interphases and the kinetics and thermodynamics of processes occurring in these regions. These new capabilities and the resultant understanding will allow development of a rational basis for chemical and physical modification of surfaces to achieve desired interphasial behavior as needed in many relevant areas including chemically selective sensors and waste processing.

Technical Accomplishments

Specific activities during FY 1994 have included completing the experimental setup and beginning model studies on liquid/liquid interfaces and colloid dynamics, and setting up a spectroelectrochemistry laboratory. Surface analysis of important oxide, sensor, and mineral interfaces was also conducted.

Scanning Probe Microscopy and Liquid/Liquid Interfaces

The purpose of this activity was the development of a scanning probe system and other techniques to study adsorption at liquid/liquid interfaces. The scanning probe microscope allows examination of adsorbates at a microscopic level; electrochemical methods supply information about average transport and adsorbate properties, and surface tension measurements (drop shape analyses) provide information about the average adsorbate concentration. A new sessile drop system which accommodates the scanning probe microscope was designed and assembled, and vibration isolation of the system was completed. An electrochemical system was set up, and required software modifications were made to allow electrochemical data collection. Finally, a boroscope system for viewing the sessile drop shape was purchased.

The sessile drop system was tested using both scanning tunneling microscopy and electrochemical measurements on a model liquid interface (mercury/water). Scanning tunneling microscope studies were conducted to investigate the movement of the mercury sessile drop surface under various liquids and feedback conditions. Direct current electrochemical measurements were conducted as a function of adsorbed thiol concentration, to give information about charge transport across the adsorbate. Alternating current impedance at the liquid interface was also measured and used to model the structure of the thiol adsorbate.

Colloid Dynamics

This activity involves the measurements of fluctuations of fluorescent light to examine the mechanical and chemical interactions of micron size particles (colloids) in solution using an optical fiber.

Over the past year the experimental system has been optimized, and data collection was initiated. We have found, for the most part, Raman scattering from the optical fiber occurring at wavelengths that overlap the fluorescent emission wavelengths. This Raman scattering dominates any detectable fluorescence. We have decided, therefore, to conduct experiments using a different laser system. This new system will allow the use of fluorescent probes that emit at wavelengths sufficiently different from the Raman scattering wavelengths. This new experimental setup should give a much better insight to the behavior of colloids at the fiber-solution interface. The laboratory is currently undergoing remodeling to accommodate the new laser system, and we anticipate collecting useful data shortly after the remodeling is completed.

Spectroelectrochemistry

This activity involves developing capabilities for optical measurements of electrochemical interfaces. The primary focus initially is on a non-linear optical technique, second harmonic generation (SHG); but other measurement techniques will also be made available. Most of the equipment required for this project was ordered and received in the past year. Installation of the laser system has been delayed until the appropriate electrical power can be provided. Equipment not dependent on this installation has been tested.

Publications

D. R. Baer, M. H. Engelhard, D. W. Schulte, D. E. Guenther, Li-Qiong Wang, and P. C. Rieke. 1994. "Electron Beam Effects on (CH2)17 Self-Assembled Monolayer SiO2/Si Specimens." *J. Vac. Sci. Technol. A* 12(4).

C. Bruckner-Lea, J. Janata, J. Conroy, A. Pungor, and K. Caldwell. 1993. "Scanning Tunneling Microscopy on a Mercury Sessile Drop." *Langmuir* 9, 3612-3617.

J. Janata, C. Bruckner-Lea, J. Conroy, A. Pungor, and K. Caldwell. 1994. "Scanning Tunneling Microscopy on a Compressible Mercury Sessile Drop." *ACS Book Symposium Series 561: Interfacial Design and Chemical Sensing*, Eds., T. E. Mallouk and D. J. Harrison, 175-185.

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Presentations

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D. R. Baer, M. H. Engelhard, D. W. Schulte, D. E. Guenther, Li-Qiong Wang, and P. C. Rieke. 1993. "Electron Beam American Vacuum Society, Orlando, Florida, November.

C. Bruckner-Lea, J. Janata, J. Conroy, A. Pungor, and K. Caldwell. 1994. "Compact Layers at a Liquid Interface: A Molecular Vise System." Presented at the Gordon Research Conference on Organic Thin Films, Ventura, California, February 28-March 4.

C. Bruckner-Lea, J. Janata, J. Conroy, A. Pungor, and K. Caldwell. 1994. "Scanning Probe Microscopy on a Mercury Sessile Drop: A Molecular Vise." Presented at the 185th ECS Meeting, San Francisco, California, May 22-27.

Other Accomplishments

A senior scientist, John Daschbach, was hired to begin the spectroelectrochemistry program.

Kinetics, Scale-Up and Demonstration of Uranium Bioprecipitation Technology

Michael J. Truex and Brent M. Peyton (Process Technology and Engineered Systems)
Yuri A. Gorby (Earth and Environmental Sciences)

Project Description

Research at the USGS and PNL identified a biological mechanism to remove heavy metals from aqueous streams (Gorby and Lovley 1992; Gorby and Truex 1993). This technology uses bacteria that can use certain metal species as electron acceptors. In the process, a soluble metal is reduced and forms an insoluble compound that can be removed from solution by filtration, centrifugation, or precipitation. The technology is applicable to remediation of U, Cr, Tc, V, Co, Se, Hg, and potentially other multivalent metal species with the appropriate oxidation/ reduction potential and solubility characteristics. Maximum metal concentrations that can be biologically processed are, for example, 50 mM U, 10 mM Co, and 1 mM Cr.

To apply this concept in a flow-through reactor at full-scale, more information is needed regarding the kinetics of both the reduction reaction and the precipitation step. The objective of this project was to obtain the basic kinetic coefficients for the process using a simulated waste. These experiments will provide the data to construct a predictive model for use in defining treatability protocols, process optimization, and conceptual design.

Technical Accomplishments

Initial work was focused on obtaining the kinetic growth parameters for the metal reducing bacterium using oxidized iron as the electron acceptor. Experiments were performed to provide a baseline for further studies with uranium while avoiding generation of radioactive waste. Data was analyzed to determine conceptual designs for the bioprecipitation process, assuming that iron reduction was a good kinetic analog for uranium reduction. Experiments were performed in batch studies using a Lineweaver-Burke analysis for the Monod kinetic growth parameters. Also continuous-flow metal reduction was performed in a stirred tank reactor to determine cell yields and demonstrate long-term metal reduction activity. The maximum specific growth rate and Monod half-saturation coefficient obtained were 0.142/h and 3.42 mg/L iron. Cell yield was 0.071 mg biomass/mg iron.

Based on the kinetic growth parameters for iron, reactor configurations were assessed for use in the bioprecipitation process. A combination of a stirred-tank reactor followed by a plug-flow reactor was determined to be the best generic design for the process. Preliminary experiments with uranium and chrome confirmed that the kinetics were faster for iron reduction than for any other metal species as an electron acceptor. Thus, the growth-based reactor design is appropriate for processing waste streams where the metal to be precipitated is the dominant electron acceptor. Examples of these waste streams include industrial wash solutions and, potentially, soil leachate solutions. However, for more complex waste streams such as mine drainage, the growth kinetics are too slow for application of this design.

To address the above problems with process performance and to produce a more robust system, a different reactor configuration was designed. This system is based on using a non-growth contactor reactor that is continually amended with the metal reducers. The metal reducers are grown in a separate reactor that is easily maintained in pure culture. The cells are then contacted with the metal-laden waste and substrate to provide energy for reduction of the metal. No other growth factors (e.g., nitrogen, phosphorus, vitamins) are added in the contactor so that growth does not occur. While some bacteria in the waste stream may be able to grow under these conditions, the metal reducers dominate because they are continuously fed to maintain a high concentration. Hence, they easily outcompete other bacteria for the substrate. Kinetics for this contactor-based design are currently being investigated. The primary disadvantage to the connector design is that more biomass waste is produced. For many applications, however, this is a minor consideration and will not have a large cost impact.

Publication

M. J. Truex, B. M. Peyton, Y. A. Gorby, and N. B. Valentine. 1994. "Process Development for Uranium Bioprecipitation." In *Proceedings of Conference on Hazardous Waste Remediation*, Montana State University (in press).

Presentation

M. J. Truex, B. M. Peyton, Y. A. Gorby, and N. B. Valentine. 1994. "Process Development for Uranium Bioprecipitation." Presented at the Conference on Hazardous Waste Remediation, Montana State University, June 8-10.

Magnetic Resonance Spectroscopy

Herman M. Cho (Macromolecular Structure and Dynamics)

Project Description

This project combines the development of new magnetic resonance methods and the application of established nuclear magnetic resonance and electron paramagnetic resonance techniques in a series of experiments directed toward answering fundamental scientific questions arising in toxic waste treatment and environmental restoration and remediation.

Technical Accomplishments

An investigation of water dynamics in single crystals of the mineral milarite is continuing. Proton nuclear magnetic resonance results clearly indicate a macroscopic ordering of water molecules in the crystal lattice, with complicated and, as yet, poorly understood motional dynamics involving rotations around well-defined axes of the water molecule. Theoretical simulations demonstrated that naïve models of the dynamics of the water molecules do not account for the experimental observations.

A theoretical and experimental project to study the rates and trajectories of the motion of hydrogen in minerals continued this year. A postdoctoral fellow from the University of California, Santa Barbara, Dr. Robert Maxwell, has been assigned to perform this work. Fully protonated and partially deuterated boehmite (AlOOH) samples have been prepared and probed by x-ray diffraction and Fourier transform infrared spectroscopy, and a full set of variable temperature proton and deuterium nuclear magnetic resonance experiments initiated to determine the parameters of motion of hydrogen atoms in this material. The goal of this study is to obtain experimental information that can guide semi-empirical quantum mechanical computations of the microscopic dynamics, atomic coordinates, and potentials present in this and related minerals. For these purposes, boehmite represents both a paradigm and an ideal starting point for understanding the phenomena of water and hydrogen transport in minerals. Boehmite is also found in some Hanford tank contents, and has ion exchanging properties that suggest it can serve as a model for deducing other, more practical ion exchangers.

Much of the work in this project involves proton nuclear magnetic resonance measurements of samples containing low amounts of hydrogen. A novel variable-temperature, high-power, proton nuclear magnetic resonance probe with a low hydrogen background is under construction to facilitate these measurements. In addition, theoretical work is being performed on relaxation pathways in condensed phases, particularly external-field assisted relaxation, and on novel time-domain experiments in electron paramagnetic resonance spectroscopy and electron-nuclear double resonance spectroscopy, in an effort to expand sensitivity, resolution, and information content of magnetic resonance experiments.

Multi-component glasses that are considered candidates for vitrification of Hanford wastes are being investigated by solid-state multinuclear nuclear magnetic resonance to elucidate the following: hydration and identification of hydrous species, factors promoting phase separation and composition of phase separated components, and the low solubility of common Hanford waste elements such as phosphorus.

Interfacial phenomena at the surfaces of metal oxide and oxide-supported metal catalysts are being investigated by multinuclear, variable temperature nuclear magnetic resonance methods. Information on adsorbate conformations and dynamics is sought, with the goal of gaining insight on the reactions and processes that occur at the surface of catalysts with industrial and Hanford waste-remediation applications. A determination of the nature of the acidity, e.g., Bronsted versus Lewis, of some simple tin oxide, zirconia, and alumina catalysts is an immediate goal of this work.

Publication

J. M. Koons, E. Hughes, H. M. Cho, and P. D. Ellis. "Extracting Multitensor Solid-State NMR Parameters from NMR Line Shapes. Some Comments and Protocols." *Journal of Magnetic Resonance* (in press).

Presentation

A plenary lecture was given at the Russian Academy of Sciences Second Annual Workshop on Modern Developments of Electron Paramagnetic Resonance, in Kazan, the Russian Federation.

Materials Surface and Interface Chemistry

Charles H.F. Peden (Materials and Interfaces)

Project Description

The objective of this project was to develop a molecular level understanding of the surface structure and chemical reactivity of environmentally relevant materials. Our main efforts during the past year have been to examine and characterized the effects of oxide surface structure on the chemistry of simple probe molecules. As in the previous year we have focused mainly on two oxide systems of titanium: thin films prepared by oxidation of vacuum-deposited Ti metal on W(110), and the $TiO_2(100)$ single crystal surface.

Technical Accomplishments

Using low energy electron diffraction (LEED) we have shown that 1 to 3 ML thick TiO_x films form incommensurate trained layers on W(110). The domain sizes for these films are large compared to the oxide unit cell based on qualitative assessments of the LEED data. Auger electron spectroscopy intensity ratios for oxygen and titanium indicate that the value of 'x' is less than 2, characteristic of a reduced form of titanium oxide. Both LEED and Auger electron spectroscopy results indicate that these films are stable up to 1500K at which point they begin to form three-dimensional islands and desorb from the surface. Based on Temperature Programmed Desorption results, the interactions of water, 1-propanol, 2-propanol, and formic acid (Lewis acids) with these films suggest the films are predominately oxygen-terminated since each molecule desorbs at a temperature close to that of their respective multilayer desorption temperature without significant decomposition.

Surfaces without exposed cation sites are therefore expected to bind Lewis acids weakly. Efforts at synthesizing ordered films of greater thickness and higher oxidation state are under way. Preliminary results indicate that films on W(110) thicker than > 3 ML exhibit surface chemical properties similar to the thinner films.

The chemical interactions of water and formic acid on the $TiO_2(100)$ surface are different from those observed on the TiO_x thin films. Both molecules bind strongly to the single crystal surface, and are thermally decomposed upon heating. We attribute this difference in chemistry (from that observed from the thin films) to the influence of a high surface concentration of coordinatively unsaturated $Ti4^+$ cation sites on the $TiO_2(100)$ surface. Water desorbs from this surface at roughly 150K higher temperature than from the film. High resolution electron energy loss spectroscopy (HREELS) measurements suggest that this high temperature desorption state of water results from OH recombination. Formic acid decomposes on $TiO_2(100)$ to formate, which further decomposes at 550K to liberate carbon monoxide in the gas phase. A small amount of formaldehyde is also formed in the formate decomposition process, presumably due to the influence of surface defect ($Ti3^+$) sites.

In addition to these efforts, a new vacuum system was assembled and tested during the past year. This system is designed to interface ultrahigh vacuum surface studies with high-pressure measurements, utilizing infrared spectroscopy as the common probe of surface chemistry. A gas chromatograph is connected to the high pressure cell and an assortment of ultrahigh vacuum techniques (x-ray photoelectron spectroscopy, LEED, temperature programmed desorption, and low energy ion scrattering) will be dedicated toward examination of molecular level phenomena at oxide surfaces. Preliminary structural studies using LEED I-V analysis have begun on the ZnO(101bar0) surface.

Presentations

M. A. Henderson. 1994. "The Influence of Oxide Surface Structure on Adsorbate Chemistry: Water on TiO_2 Single Crystal Surfaces." Presented at the Gordon Research Conference, Water at Interfaces and Surfaces, Plymouth, New Hampshire, July.

M. A. Henderson. 1994. "The Influence of Oxide Surface Structure on Adsorbate Chemistry: Water on TiO_2 Single Crystal Surfaces." Presented at the Department of Chemistry, Auburn University, Auburn, Alabama, August (invited).

M. A. Henderson. 1994. "The Interaction of Water with the (100) face of TiO_2." Presented at the 207th American Chemical Society National Meeting, San Diego, California.

Microbial Genomics

Jeffery D. Saffer, Richard P. Schneider, and Richard J. Douthart (Biology and Chemistry)

Project Description

The use of microbes in biotechnology is rapidly increasing. These diverse organisms represent the majority of organisms in the world and provide a limitless resource of genetic coding information. To exploit microorganisms fully, considerable information needs to be learned about their function and genetic coding capacity. This project uses genomic studies to provide a genetic basis for bioremediation and other biotechnological applications.

Most enzymatic activities of use in bioremediation are plasmid-borne. In addition, biodegradative genes on plasmids are usually organized into polycistronic units; this organization facilitates identification of other genes in the pathway of interest. Therefore, these studies focus on plasmids within bacteria of interest. Through physical mapping and sequencing progress can be made in fundamental areas such as plasmid genetics, gene organization, element mobilization, and plasmid transfer.

PNL scientists have isolated a *Pseudomonas*-like bacterium from the deep (400 m) subsurface (*Appl Env Microbiol* 57:796, 1991). This bacterium, F199, is uniquely able to biodegrade an array of aromatic hydrocarbons including toluene and naphthalene. Furthermore, F199 can function under microaerophilic conditions making it especially suitable for bioremediation.

F199 harbors at least one very large plasmid (>100 Kb). The plasmid(s) appears to be stable even without selective pressure suggesting that some essential functions may reside on these extrachromosomal DNA segments.

The goal of this project was to generate a physical map of the F199 plasmid that is sufficiently detailed to facilitate localization of new genes (Figure 1).

Technical Accomplishments

In the past year, we have made significant progress in these genomic studies. The genome of F199 has been characterized and was found to contain three genetic elements of 2 Mb, 500 Kb, and 180 Kb.

To characterize the 180 Kb plasmid, it was first necessary to adapt plasmid isolation techniques for successful isolation of high molecular weight DNA (Figure 2). Success in this endeavor has allowed us to prepare large amounts of pure plasmid needed for analysis and cloning.

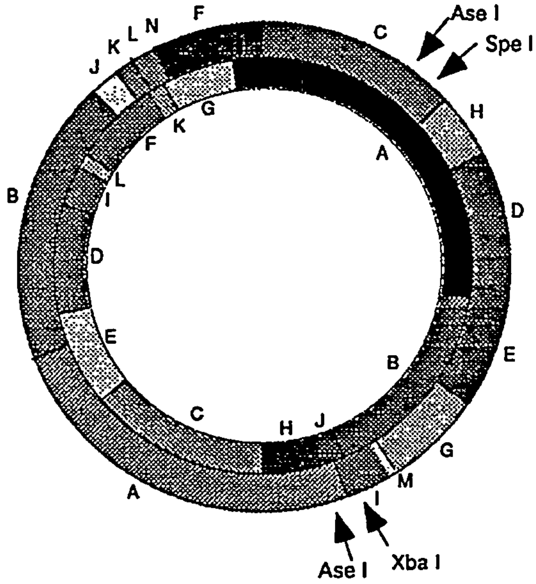

Figure 1. Physical Map of the F199 Large Plasmid

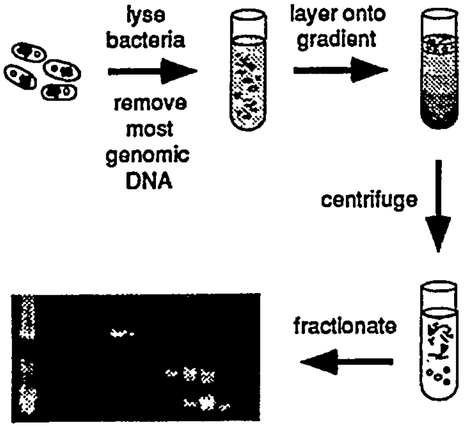

Figure 2. Purification Scheme for Large (>100 Kb) Plasmids

A cosmid library of the plasmid sequences was constructed to provide easy access to different regions of the large plasmid and to facilitate generation of a physical map. Approximately 300 individual clones were made, providing coverage of the entire plasmid.

Digestion of the cosmid clones with restriction endonucleases was used to determine which cosmid clones overlapped each other and then define the order of all the clones. This information also led to a restriction map of the entire plasmid. In addition, pulsed field electrophoresis was used to locate the cleavage sites for restriction enzymes that cut the plasmid infrequently.

The cosmid clones were analyzed to determine which ones contained the gene for catechol-2,3-dioxygenase, an enzyme central to the pathway for degrading aromatic hydrocarbons. Several cosmids were identified and the regions of each that overlapped were used to localize this gene. DNA sequence was derived from this region and confirmed that a catechol-2,3-dioxygenase gene was present on the large plasmid.

To handle the large amount of information derived from genomic studies, appropriate informatics tools have to be developed for the presentation and analysis of microbial genomics data. Work has proceeded in this area by identifying what the needs are and what tools already exist.

Publication

R. P. Schneider, L. C. Stillwell, S. J. Thurston, M. F. Romine, J. K. Fredrickson, and J. D. Saffer. "Characterization of a complex genome from the deep subsurface *Sphingomonas* F199." (in preparation).

Presentation

L. C. Stillwell, R. P. Schneider, J. K. Fredrickson, M. F. Romine, and J. D. Saffer. 1994. "Isolation and characterization of a 180Kb plasmid from the subsurface bacterium F199." Presented at 94th Annual Meeting of the American Society for Microbiology, Las Vegas, Nevada.

Molecular Visualization on Parallel Computers

Randy W. Heiland (Information Systems and Engineering)

Project Description

The objective of this project was to develop portable parallel rendering algorithms. The second phase of the project will be to write a design document for a parallel ray-casting volume renderer. The third phase will be to prototype and develop the code. This will include making use of the parallel programming libraries, Global Arrays and TCGMSG. The final stage will be to write a paper describing results from using the renderer for chemistry-related datasets. An implicit objective of this work is to expand our expertise in writing parallel applications.

Scientific visualization encompasses many computer-graphical techniques for displaying scientific data. When multiprocessor or distributed computing architectures are applied to science and engineering problems, the resulting dataset sizes can become quite large. It is only natural to apply multiprocessor (parallel) visualization algorithms to such data, which is the goal of this project.

Volumetric scientific datasets can be divided into two types, scalar and vector. (By 'vector' we mean the classical definition of data with magnitude and direction; hence, describing dynamical behavior.) For this project we concentrate on scalar data, i.e, $f(x,y,z)$, where f is a scalar function. An alternative to volumetric data is data consisting of geometric primitives. For example, in molecular sciences, a common visualization is the ball and stick method consisting of spheres (atoms) and cylinders (bonds).

A graphical representation which can be applied to both volumetric and geometric primitive datasets is a surface representation. In volumetric data, one can, for example, construct an isosurface ($f(x,y,z) = \text{constant}$). Geometric primitives have inherent analytic surface shells. In computer graphics, it is quite common to construct and display (render) surfaces using polygons.

A visualization technique quite different from surface rendering is known as volume rendering. Rather than display distinct surfaces, this technique produces an image of the entire volumetric dataset as a translucent (jello-like) projection. Parameters that determine the color and opacity of particular ranges of scalar values can be adjusted to highlight certain features of the data.

Technical Accomplishments

Progress made to date has focused on polygon rendering of surfaces in three-dimensional space. Software development has evolved as follows:

- an image decomposition rendering algorithm was implemented using a platform-independent message-passing library called TCGMSG. This was initially run on the Intel Delta machine at Caltech and local distributed UNIX (Silicon Graphics) workstations.
- an object decomposition rendering algorithm was implemented using a platform-independent shared-memory programming toolkit called Global Arrays. The primary architecture targeted for testing this algorithm was the Kendall Square KSR2 multiprocessor.

Due to the full-image composition scheme being used by the latter rendering algorithm, scaling results were encouraging only up to about eight processors. Above this, communication costs were too great. Techniques for improving on this will be addressed in future work. The implicit objective of this project was to expand our expertise in writing parallel applications and this has been and continues to be accomplished.

Publication

R. W. Heiland. 1994. "Object-Oriented Parallel Polygon Rendering." In *Proceedings of GVis '94;* p. 19-26. Richland, Washington.

Presentation

R. W. Heiland. 1994. "Parallel Rendering Activities at PNL." Presented at the DOE Computer Graphics Forum, April 26, Rocky Mountain National Park, Colorado.

Multinuclear Solid-State NMR Characterization of the Early Forms of Mineralization

Paul D. Ellis (Macromolecular Structure and Dynamics)

Project Description

Early phases of bone formation will be investigated by multinuclear (i.e., ^{1}H, ^{13}C, ^{31}P, ^{113}Cd) solid-state nuclear magnetic resonance spectroscopy. These data will prove to be essential for the determination of the possible role of octacalcium phosphate as a precursor phase in apatitic lattice formation. The results of this research will have significant impact on our understanding of the details of bone formation and on the synthesis and characterization of bio-materials. Likewise, such research will provide valuable insight into what processes are being altered when developing bone is exposed to toxic chemicals and/or radiation.

Technical Accomplishments

The main objective of the proposed research is to characterize the phases present in "normal" and "developing" bone. A knowledge of these phases will be essential in the understanding of transformations in bone material as a result of chemical or radiation exposure or normal aging. As the principal spectroscopic tool for this investigation we will use multinuclear solid-state nuclear magnetic resonance (NMR) spectroscopy. The crystal structure of the principal component of bone, hydroxyapatite (HAp) i.e., $[(Ca_{10}(PO_4)_6(OH)_2)]$, is known. Bone itself is known to be a disordered structure based upon the hydroxyapatite structure. The disorder is mainly associated with the population of the Ca^{2+} sites and the sites of protonation of the various phosphate groups. Hence, the ideal probe for studying bone structures would be ^{43}Ca nuclear magnetic resonance. However, in part because of its quadrupolar nature ^{43}Ca is exceptionally difficult to study with nuclear magnetic resonance. Therefore, it will be investigated whether we can replace the calcium in the lattice by cadmium, and utilize ^{113}Cd nuclear magnetic resonance as a surrogate probe for Ca^{2+} sites. Further, hydroxyapatite has the complication that the hydroxyapatite lattice can "slip" into a octacalcium phosphate, octacalcium phosphate, phase.

Recently a ^{1}H-^{31}P double resonance study was carried out on bone, and indications were found of the existence of this phase in bone (R. A. Santos, R. A. Wind, and C. E. Bronnimann, *J. Magn. Res. B* [in press]). It will be investigated whether ^{113}Cd nuclear magnetic resonance and ^{1}H-^{113}Cd as well as ^{31}P-^{113}Cd double resonance nuclear magnetic resonance can confirm these findings.

Given the complicated structure of bone minerals, it is essential to perform nuclear magnetic resonance on model compounds as well. We now can routinely synthesize hydroxyapatite and octacalcium phosphate, and we recently succeeded in synthesizing cadmium substituted hydroxyapatite as well. As a start, we investigated these compounds by ^{1}H nuclear magnetic resonance spectroscopy, specifically ^{1}H CRAMPS (i.e., Combined Rotation and Multiple-Pulse Spectroscopy). The method utilizes multiple pulse methods in addition to magic-angle spinning to narrow the ^{1}H line width sufficiently to achieve "functional group resolution" in the nuclear magnetic resonance spectrum (i.e., water groups from hydroxyl [OH] groups, etc.). Figure 1 shows the octacalcium phosphate ^{1}H CRAMPS spectrum of hydroxyapatite.

The resonance centered at 6 ppm is that of adsorbed water and water in the lattice, the line at 0.2 ppm originates from the hydroxyl apatitic protons. Octacalcium phosphate normally shows an extra acid proton peak at 12 ppm, if it is present.

Figure 2 shows the ^{1}H CRAMPS spectrum of the Cd-substituted hydroxyapatite. Note the shift in the water resonance, from 6 to 4 ppm. Most, if not all of this water is water within the lattice.

We also performed ^{113}Cd nuclear magnetic resonance spectroscopy on the Cd-substituted hydroxyapatite. The ^{113}Cd spectrum only shows one broad resonance line. Its width is indicative of a disordered environment. Finally, we performed ^{1}H-^{31}P CPMAS (cross-polarization combined with magic-angle spinning) experiments in hydroxyapatite with different percentages of Cd substitutions. We found a small change in the isotropic chemical shift of the ^{31}P resonance. The origin of this shift is not precisely known at this moment and is the subject of further investigations.

We know from the crystal structure of the of hydroxyapatite that there are two types of Ca^{2+} sites in the lattice. They appear as two concentric circles of Ca^{2+} sites within the lattice. The distance between the outer ring of Ca^{2+} and its closest phosphorous atom is 3.22Å and the distance between the close phosphorous and the inner Ca^{2+} ion is 3.67Å. We should be able to demonstrate that both Cd^{2+} are in those sites by performing a $^{31}P \rightarrow {}^{113}Cd$ cross-polarization experiment in the

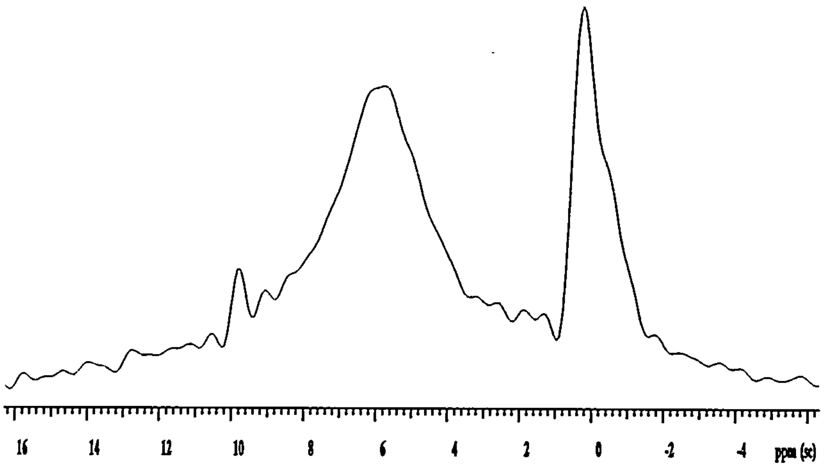

Figure 1. ^{1}H CRAMPS Spectrum of Hydroxyapatite

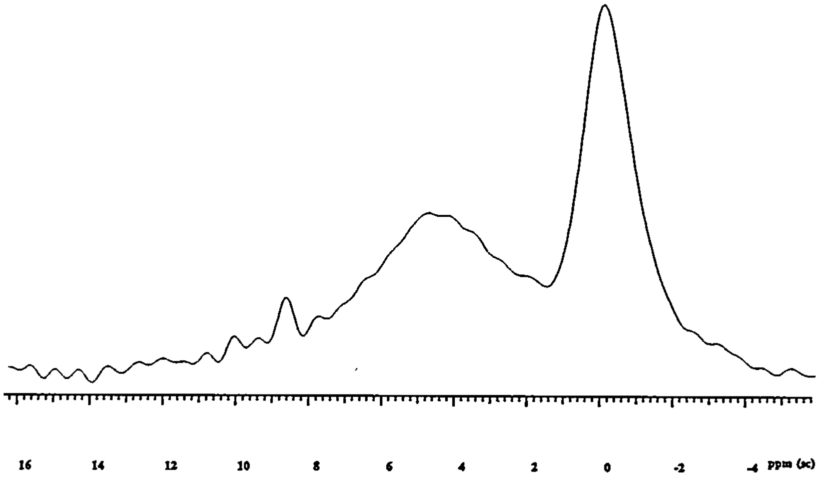

Figure 2. ^{1}H CRAMPS Spectrum of Cd-Substituted Hydroxyapatite

Cd-substituted hydroxyapatite. If the same difference in distance occurs in this compound, we can perform a variant of the cross polarization experiment which will make it possible to discriminate one site over the other—even though they possess nearly identical chemical shifts. Hence, we will have spectroscopic labels for the protons, phosphorus, and calcium sites in hydroxyapatite, octacalcium phosphate, and any form of the bone.

Such experiments will form the basis of this coming year's research activity.

Presentation

P. D. Ellis, A. S. Lipton, K. McAteer, B. A. Concannon, S. Mason, R. Wuthier, D. Reger, R. A. Santos, and R. A. Wind. 1994. "Recent Progress in ^{113}Cd NMR of Biological Systems." Presented at the 36th Rocky Mountain Conference, Denver, Colorado.

Neural Network Data Processing for Sensor Applications

Richard T. Kouzes (Computing and Information Sciences)

Project Description

The objective of this project was to demonstrate the potential data processing capabilities of neural networks in sensor applications. This effort concentrated on the problem of identifying objects in the environment from their sensor signatures. This work developed neural network techniques for automated sensing applications and evaluated whether the neural network approach is beneficial to these applications.

There are many real-time and remote sensing applications that require an inexpensive, compact, and automated system for identifying an object (e.g., target, chemical, isotope). Such a system could be constructed with a sensor array and an automated pattern recognition system (such as a neural network). The current trend in sensor technology is to build arrays of sensors with each element keyed to a different response. The quantity and complexity of the data collected by these sensor arrays can make conventional analysis of the data difficult. Neural networks, which have been used to analyze complex data and for pattern recognition, could be a better choice for sensor data analysis. While most areas in sensor technology are mature, the application of neural network technology to real-world problems is relatively new. Application of the pattern recognition capabilities of neural networks to automated identification of objects from their sensor signatures is still in its infancy, and we are advancing this frontier.

An artificial neural network is a computing architecture derived from a rudimentary understanding of the brain. It is basically an information processing paradigm composed of a large number of highly interconnected processing elements (neurons) working in unison to solve specific problems and can be implemented in either hardware or software. Artificial neural networks are generally used in pattern recognition, prediction, decision making, and optimization. Neural networks have been applied to a few sensor analysis problems. One application is the recognition of the chemical composition of a vapor. Sensor arrays coupled with artificial neural networks that perform automated chemical classification are often referred to as artificial or electronic noses. Several applications of this kind include monitoring food and beverage odors, automated flavor control, analyzing fuel mixtures, discriminating the smoke from different brands of cigarettes, detecting oil leaks, identifying different types of alcohol, and quantifying individual components in gas mixtures. Another application is in determining the radioactive isotopes in a sample from their gamma ray spectra.

Technical Accomplishments

A literature search on the use of neural networks in sensor analysis was performed and we have studied some of the approaches. We have developed contacts with other groups in the U.S. (Los Alamos National Laboratory, Honeywell Technology Center, University of Maryland, and Colorado School of Mines) working on artificial neural network-based sensor analysis.

One of the objectives of this project was to identify and evaluate applications of this technology on the Hanford Site. As part of this effort, we hosted a neural network workshop on January 26, 1994. Another workshop is anticipated for FY 1995.

As part of our effort to develop collaborative efforts with the outside world and to provide an informal level of peer review, we developed a World Wide Web (WWW) server on the field of neural networks that can be viewed by anyone on internet through a World Wide Web client such as Mosaic. This server contains descriptions of our work, associated papers, and hypertext links to other groups performing similar research around the world. From this server, we have established many contacts.

A portion of this project has involved continued evaluation of local applications of our ideas. We are developing three prototype systems for initial implementation, and will continue to explore others. From the neural network workshop that we hosted in January, additional applications including automated inspection of 210-liter drums used in low-level nuclear waste storage, analysis of arc spectroscopy, and automated examination of soil contamination were identified.

The main portion of our research effort is the development of three prototype artificial neural network systems that process real sensor data. A prototype system consists of a sensor array, data acquisition system, a desktop computer, and an artificial neural network implemented in software. In these systems, the artificial neural network is used to identify the composition of the sensed analyte. With a neural network, the intense computation takes place during the training process, and operation of the system can take place in real-time.

The first system employs an array of tin-oxide chemical sensors and is used to identify chemical vapors. This system was constructed during FY 1994. A system of this kind is sometimes known as an artificial or electronic nose. The second prototype, an optical system, was constructed during FY 1994 in cooperation with the Sensor Physics group in PNL. This system will be used to identify the composition of chemical dyes in liquids. The third prototype is for gamma ray spectrometry used to identify radioactive isotopes, and software for this prototype has been developed.

Each analyte (i.e., chemical vapor, chemical dye, isotope) presented to the sensor array produces a signature or pattern characteristic of that analyte. By presenting many different known analytes to the sensor array, a database of signatures can be built up. Labeled patterns (i.e., patterns from known analytes) are used to train the network. The goal of the training is to learn an association between the sensor array patterns and the labels representing the data. Once the network is trained, operation consists of propagating the data through the network. Various neural networks, including backpropagation, linear vector quantization (LVQ), optimal linear associative memory (OLAM), and Hamming-Net, will be explored for these prototypes. During FY 1994, the backpropagation and OLAM algorithms were implemented and tested.

Evaluation of these prototypes consists of presenting the systems with mixtures of analytes and comparing the response of the network to the known composition of the mixture. Depending on the results we obtain, modifications to the training procedure could be implemented as part of this effort. During FY 1994, the artificial nose was tested with eight common household chemicals. During FY 1995, mixtures of analytes will be tested with the artificial nose. The software for the radioactive isotope sensing system was tested with gamma-ray spectra of eight radioactive isotopes along with mixtures of these isotopes. Also, alpha-particle spectra provided by Westinghouse Hanford Company were examined with an artificial neural network for identifying spectral quality.

Publications

L. J. Kangas, P. E. Keller, S. Hashem, and R. T. Kouzes. 1994. "Alpha Spectral Analysis Via Artificial Neural Networks." In *Proceedings of the Nuclear Science Symposium*, Norfolk, Virginia.

P. E. Keller and R. T. Kouzes. 1994. "Gamma Spectral Analysis Via Artificial Neural Networks." In *Proceedings of the Nuclear Science Symposium*, Norfolk, Virginia.

P. E. Keller, R. T. Kouzes, and L. J. Kangas. 1994. "Neural Network Based Chemical Sensors for Environmental Monitoring." In *Proceedings of the World Congress on Neural Networks*, San Diego, California.

P. E. Keller, R. T. Kouzes, and L. J. Kangas. 1994. "Neural Network Based Sensor System for Manufacturing Applications." *Proceedings of the Conference on Advanced Information Systems and Technology for Acquisition, Logistics and Personnel Applications*, Williamsburg, Virginia.

P. E. Keller, R. T. Kouzes, and L. J. Kangas, Editors. 1994. *Proceedings of the Neural Network Workshop for the Hanford Community*, Richland, Washington.

P. E. Keller, R. T. Kouzes, and L. J. Kangas. 1994. "Three Neural Network Based Sensor Systems for Environmental Monitoring." In *Proceedings of the IEEE Electro '94 Conference*, Boston, Massachusetts.

Presentations

S. Hashem, P. E. Keller, R. T. Kouzes, and L. J. Kangas. 1994. "Neural Network Based Data Analysis For Chemical Sensor Arrays." Submitted to the Artificial Intelligence Research in Environmental Science conference, Biloxi, Mississippi.

P. E. Keller, R. T. Kouzes, L. J. Kangas, and S. Hashem. "Transmission of Olfactory Information for Telemedicine." Submitted to Medicine Meets Virtual Reality III, San Diego, California (January 19-22, 1995).

Other Accomplishments

P. Keller, the postdoctoral fellow who carried out this work this year, became a PNL staff member.

Professor Thomas P. Lofaro of Washington State University was a summer fellow at PNL participating in this work.

North American 3E Model

James A. Edmonds (Global Environmental Management)

Project Description

The goal of this research was to develop and test an integrated and quantitative model of the North American economic-energy-environmental system (i.e., NA3E Model). This model stands on its own as an independent computational tool and is directly useful to continued development of the PNL Second Generation Model (the NA3E model will integrate the U.S., Mexican, and Canadian modules of the Second Generation Model). The overall Second Generation Model architecture is designed so that models can be integrated without any changes in either system boundary definitions or computer code.

The NA3E model will be used to project future features of the North American economic-energy-environmental system in sufficient detail to permit evaluation of various aggregate policies and practices relevant to sustainable development trajectories. Attention will be focused on how near-term energy, environmental, and economic decisions will affect the evolution of the increasingly integrated North American energy system, which is the focus of significant current attention due to developments such as the North American Free Trade Agreement (NAFTA).

A key element of this project was to develop specific research collaborations with organizations in the U.S., Canada, and Mexico using existing contacts with North American energy and environmental experts.

The specific knowledge developed from each of the five project tasks will also be integrated into an expanded version of the Second Generation Model, and tailored to the current situation in North America. The resulting modeling capability will be unique among global environmental analysis tools and could have major application in supporting U.S. government and private sector decisions related to competitiveness, trade, energy, and environmental policy issues.

Technical Accomplishments

Integrating Technological Changes and Policy Decisions Affecting the United States

Significant progress was made in this task on two fronts. First, a workshop was conducted which brought together participants from the 1993 Aspen Institute Workshop on Energy to assess the feasibility of using the Aspen workshops as a source of technological and policy information for modeling. Hugh Pitcher presented early results of analysis using the Second Generation Model to quantify issues raised at the 1993 Aspen Institute. Workshop participants endorsed the continued development of a quantitative representation of their 1993 work. Paul Runci, John Clarke, and Chester Cooper have worked jointly on this element of the project.

Second, a paper was prepared for the 1994 Aspen Institute Workshop on energy summarizing the long-term consequences of technological and resource issues discussed at the 1993 Workshop. A final version of the paper is nearly complete.

Mexico

This task supported the development of an energy economy module within the Second Generation Model framework for Mexico. A collaborating team, led by Dr. Jaime Matus, has been developing data for model calibration. A second meeting was held in early August to further develop the data sets. All necessary data except for the detail on the composition of the electricity sector has been collected and put into a format suitable for input into the calibration process.

Canada

This task supported the development of an energy economy module within the Second Generation Model framework for Canada. The collaborating team, which was led by Dr. Hans Hoelger Rogner, has completed work on the calibration database for the Second Generation Model. Work on the reference scenario has produced a preliminary reference scenario.

Ecological Baseline and Responses to the Growth of a North American Energy System

The "environment E" component contributes to the NA3E project through two linked activities:

- Development of a continentally coherent and geographic information system-mappable information base on soils, climate, water resources, land use, physical infrastructure, and other relevant factors to facilitate identification of specific regions, localities, and enterprises that may be affected by the implementation of NAFTA, as well as by other potential changes, as for example, climate change.

The geographic information system framework has been installed at PNL's Battelle Washington D.C. Office, and baseline data for the three NAFTA countries have been incorporated. In each country, data on soils, elevation, land use, land cover, and climate are being accessed by our collaborators for inclusion in the GAS.

- Development of a capability for process simulation modeling of North American agriculture, water resources, forestry, and unmanaged ecosystems that will make use of and contribute to the information base.

The objective of the agricultural productivity modeling work was to demonstrate the capacity of the consortium to simulate current potential and actual agricultural productivity for the major crops in Canada, the U.S., and Mexico and their sensitivity to environmental and economic change. Representative farms were designed to typify the important agricultural regions, the current crops, and agricultural technologies in use on the North American continent. Current productivity of these representative farms in terms of biomass and harvestable yields, as well as water use (evapotranspiration) was simulated by means of the Erosion Productivity Impact Calculator (EPIC) model developed by Texas A&M University. Thus far, about 100 such farms growing corn, soybeans, sorghum, winter and spring wheat, rice, alfalfa, cotton, and range grasses have been developed for the United States. Fifteen representative farms growing winter wheat, spring wheat, barley, and canola have been developed for Canada. Work is beginning in Mexico at this time.

The objective of the stream flow modeling effort was to develop a tori-lateral capability to simulate impacts of natural and anthropogenically forced environmental change and NAFTA policy-driven change on the water resources of the North American continent at a level of detail consistent with the needs of integrated assessments. We plan to apply the Soil Water Assessment Tool and Hydrologic Unit Model for the U.S. to all three countries. Hydrologic modeling work will begin on a few selected watersheds in Mexico and Canada once the GAS is fully developed to include these countries. HUMUS modeling for the entire United States has already begun and preliminary results are being checked against measured stream flows in selected basins and against estimates of natural stream flows produced by other means.

To accomplish these objectives, we formed a trilateral consortium of scientific institutions including the Atmospheric Environment Service and Inland Waters Directorate (units of Environment Canada), the University of Alberta, the Post Graduate College, Mexico City, the Mexican Institute of Water Technology, the Mexican Agricultural Research Service, the Integrated Information Management Laboratory of Texas A&M University and Pacific Northwest Laboratories.

Presentations

UCAR's Global Change Institute on Integrated Assessments, Snowmass, Colorado, summer 1994.

U.S. Global Change Research Program briefing

Social Sciences Research Council 1994 meeting in Washington, D.C.

Aspen Institute: Forum on Public Policy Issues of Energy and Resources

NMR Studies of Altered-DNA/Protein Complexes

Michael A. Kennedy (Macromolecular Structure and Dynamics)

Project Description

The objective of this project was to develop capabilities for nuclear magnetic resonance structure determination of proteins and peptides. We have initially chosen a 21-residue antigenic peptide which has potential application in treatment, prevention, and autoregulation of experimentally induced encephalomyelitis. We illustrate how circular dichroism spectroscopy can be used to determine under what conditions peptides and proteins assume structure amenable for nuclear magnetic resonance investigations. The capabilities being developed will be applied to structural studies of DNA repair proteins and transcription factors and their complexes with damaged DNA. A knowledge of how proteins recognize and interact with damaged DNA will provide a fundamental understanding of DNA repair, gene regulation in the presence of DNA damaged promoters, and DNA translational synthesis.

Technical Accomplishments

This year, we have begun to focus on peptide and protein structure using nuclear magnetic resonance spectroscopy. While our main thrust is toward understanding DNA/protein interactions, DNA protein complexes are rather large for nuclear magnetic resonance studies. In order to develop our protein nuclear magnetic resonance structure determination capabilities, we initially chose to study a rather small, synthetic T cell receptor (TCR) V region peptide that has been used for prevention, suppression, and treatment of experimental autoimmune encephalomyelitis (Vandenbark et al., Oregon Health Science University, Portland). The effectiveness of synthetic peptides as a therapy for experimental autoimmune encephalomyelitis and multiple sclerosis depends on binding constant of the peptide to the secondary antibody. Researchers are currently considering variation of the amino acid sequence of the T cell receptor peptide to enhance binding; however, no structural data was available until now. We have set out to determine what structural propensity is present in this relatively short peptide that is unique to the $V_{\beta}8_{39\text{-}59}$ fragment of the primary antibody.

Nuclear magnetic resonance studies of peptides frequently take advantage of the propensity of the peptides to assume structure in the presence of the organic solvent trifluoroethanol (TFE). Figure 1 shows the circular dichroism spectra of $V_{\beta}8_{39\text{-}59}$ as a function of trifluoroethanol concentration. Up to 20% trifluoroethanol concentration, there is little or no indication of secondary structure, but at 30% the rotation of light at 210 nm and 220 nm clearly indicates a distinct secondary structure has been assumed.

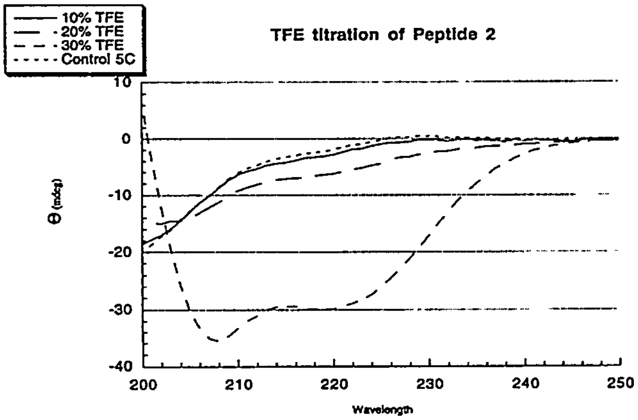

Figure 1. Circular Dichroism Spectra of $V_{\beta}8_{39\text{-}59}$ as a Function of Trifluoroethanol Concentration

In order to further investigate the structured peptide, the synthetic peptides in nuclear magnetic resonance quantities were acquired. Figure 2a shows the one-dimensional nuclear magnetic resonance spectrum in the amide and alpha proton region of $V_{\beta}8_{39\text{-}59}$ in 90% H_2O. Both the amide protons (6.5 ppm to 9.0 ppm) and the alpha protons (3.8 ppm to 4.8 ppm) exhibit narrow lines and frequency dispersion that is typical of a random coil in solution. However, in 30% trifluoroethanol, (Figure 2b) the lines become broad and the chemical shift dispersion for both amide and alpha protons collapses as expected in the case of alpha helix structure.

The next step in three-dimensional structure determination by nuclear magnetic resonance is proton assignments. We are making initial proton assignments in the random coil sample in the absence of trifluoroethanol. These assignments will be useful when comparing the "structured" peptide with the random coil peptide, i.e., those residues which remain unstructured will not be expected to experience significant chemical shifts in contrast to residues that occur in structured regions. Two nuclear magnetic resonance experiments are useful in this regard. The water NOESY experiment allows sequential assignment of (n)-alpha to (n+1)amide protons and water TOCSY experiments allows assignment of amino acid spin systems by identifying all protons that are within three to four chemical bonds. Figure 3a shows the water NOESY for $V_{\beta}8_{39\text{-}59}$. All 21 amide protons appear

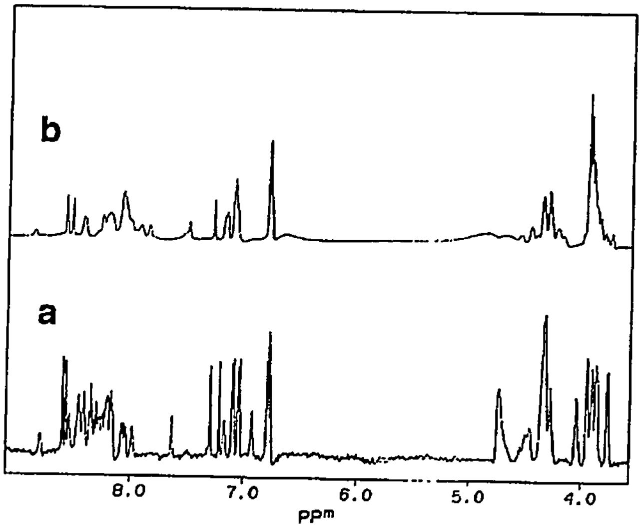

Figure 2. One-Dimensional Nuclear Magnetic Resonance Spectrum of $V_{\beta}8_{39-59}$ in (a) 90% H_2O and (b) 30% Trifluoroethanol in H_2O

resolved in the amide (D1, 7.8 ppm) to alpha (D2-3.7 ppm to 5.0 ppm) interresidue crosspeak region.

Additionally, many amide (D1, 7.8 ppm) to beta, gamma, etc., crosspeaks are apparent in the water NOESY and are useful for making proton assignments. Figure 3b shows a water TOCSY in the same region as the water NOESY. Both spectra illustrate that this peptide shows good chemical shift dispersion in amide and alpha regions and should be assignable using conventional methods for unlabeled proteins.

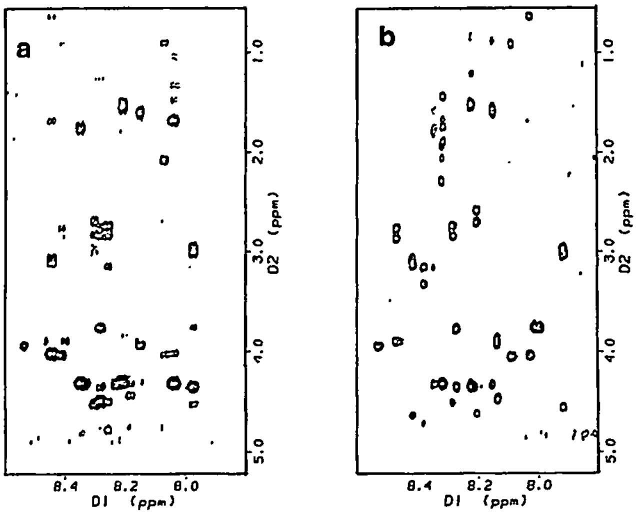

Figure 3. Amide to Alpha, Beta, Gamma, Delta Region of (a) Two-Dimensional-Water NOESY and (b) Two-Dimensional-Water TOCSY

We are currently completing assignment of the peptide in water and are collecting nuclear magnetic resonance data for the structured peptide in 30% trifluoroethanol.

Subsequent to making proton assignments, we plan to complete the structure determination of the structured peptide. These data provide the first insight into the structure of these potentially useful therapeutic antigenic peptides in the treatment of experimental autoimmune encephalomyelitis and multiple sclerosis-related disease.

Publications

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Presentations

B. D. Thrall, D. L. Springer, and M. A. Kennedy. 1994. "Structural Studies of Sequence-Specific Benzo[a]pyrene Diol Epoxide Adduct Formation." Presented at the Annual Meeting of the Environmental Mutagesis Society, Portland, Oregon, May 7-12.

NMR Studies of DNA Structure Associated with Chemical Adduction

Michael A. Kennedy (Macromolecular Structure and Dynamics)

Project Description

The objective of this project was to determine the local and secondary structural features of "G:C rich" sequences of DNA that could explain the unusually high and stepwise pattern of benzo[a]pyrene diol epoxide adduction that occurs in the 5' to 3' direction in poly-dG DNA. The molecular level understanding of this process will provide valuable insight for explaining or predicting chemical adduct formation to DNA for benzo[a]pyrene diol epoxide and other potential and established carcinogens. Knowledge of the secondary structure surrounding the adduct is needed to realize the potential disruption of normal gene regulation in damaged poly-dG transcription factor binding sites, for understanding the damage recognition and repair or misrepair, and translesional synthesis products.

Technical Accomplishments

Exposure of the human genome to carcinogenic chemicals or radiation leads to the formation of chemical adducts directly bound to DNA or to chemical alterations to nucleotide structure, respectively. The deposition of chemical adducts is, in general, nonrandom depending on local sequence and its immediate sequence context whereas the deposition of radiation-induced lesions does not appear to be directly affected by sequence. Once stable adducts or lesions are formed, how the repair efficiency, translesional synthesis, and binding of regulatory proteins to their operator sequences depends on local structure (presentation of functional groups and topology), sequence context, and stereochemistry is unknown.

During FY 1994, we investigated the structural aspects of local DNA sequence in order to understand the mechanism of benzo[a]pyrene diol epoxide (BPDE) adduction to DNA. Covalent adduct formation by BPDE is sequence-dependent with enhanced binding in poly-dG sequences. This is significant because the regulatory sequences of many genes are G:22 C-rich and adduct formation in such sequences might disrupt normal gene regulation. Not only is BPDE binding enhanced in poly-dG regions, but the adduction within a poly-dG sequence is greater in the 5' guanines than in the 3' guanines. DNA accommodation of the predominant BPDE adduct requires a widening of the DNA minor groove; thus, variations in groove width might contribute to sequence-dependent adduction. Previous nuclear magnetic resonance studies of poly-dA sequences show that the minor groove is progressively narrower toward the 3' DNA end. A similar effect in a run of guanines might explain the pattern of BPDE adduct formation observed. To examine this possibility, we studied the structure and adduct formation in a series of 12 base-pair DNA sequences in which a guanine replaced an adenine in a central run of adenines. In DNA, the minor groove width can be indirectly measured by nuclear magnetic resonance spectroscopy via a direct measurement of the (n)-adenine-H2 to (m+1)-sugar-H1' distance (which is correlated with the minor groove width) by integrating a nuclear Overhauser effect crosspeak in a two-dimensional nuclear magnetic resonance spectrum. In order to estimate the minor groove width at the guanine residue, the minor groove width at the adenine residues immediately preceding and following the inserted guanine was measured.

In Figure 1, we compare the two-dimensional NOESY (n)-adenine-H2 to (m+1)-sugar-H1' crosspeak intensities

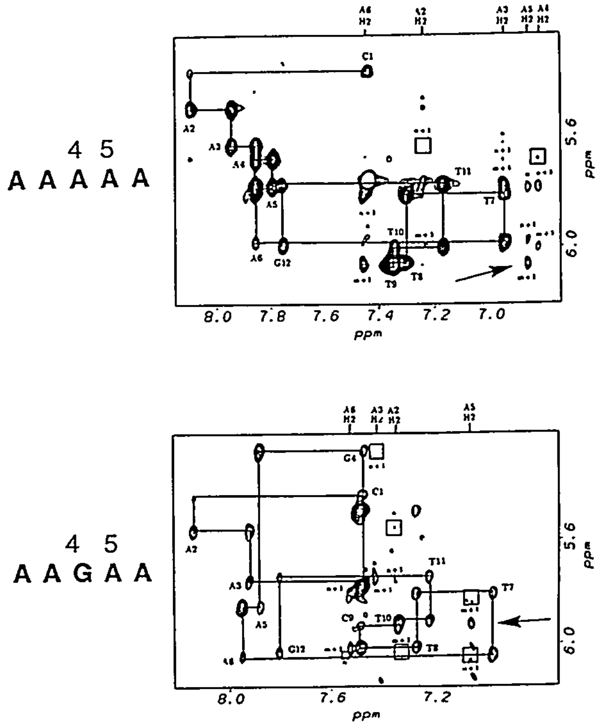

Figure 1. Contour Plots of the Aromatic to H1' Region of a Two-Dimensional NOESY

in CAAAAATTTTTG where a gradual compression of the minor groove has been previously observed (Figure 1, top panel) with those in CAAGAATTCTTG, where a guanine has been inserted at the A5 position (Figure 1, bottom panel). In the control sequence, the arrow (Figure 1, top panel) indicates the A5-H2 to (m+1)-H1' crosspeak intensity corresponding to a distance of about 3.8 A. In the G-inserted sequence (bottom panel, Figure 1), the arrow indicates that the A5-H2 to (m+1)-H1'crosspeak intensity is not altered by an inserted G at the 3 position. These data suggest that, contrary to past predictions, guanine residues can be accommodated into a narrow minor groove structure despite the presence of the exocyclic-2-amino group. Given this evidence for narrow minor groove formation in poly-dG sequences, we would predict that BPDE adduction in these "G insert" sequences should vary with the position of the guanine residue.

We measured the BPDE adduction yield for five members of the "G insert" series. When guanine is positioned near the 5' end of the DNA sequence, based on nuclear magnetic resonance results, we expect the minor groove to be wide. Since BPDE adduction requires a widening of the minor groove in B-DNA, we predict the highest yield of BPDE adducts when guanine is situated near the 5' end of the sequence. In contrast, where guanine is situated near the 3' end of the DNA sequence, we expect the minor groove to be narrow and BPDE adduct yield to be low. As expected, there is nearly a fourfold increased yield of BPDE adducts when the guanine is situated near the 5' end of the DNA sequence in TATAGAAATTTCTATA (2.52%) when compared to a guanine situated near the 3' end of the DNA sequence in TATAAAAGCTTTTATA (0.65%).

In order to better understand how guanines are accommodated into a narrow minor groove structure, we have performed molecular mechanic/dynamics calculations on a model sequence CGCAAAAGAAAAGCG. In Figure 2, the (n)-H(N)2 to (m+1)-H1' distance is plotted as a function of nucleotide number.

The general compression of the minor groove, indicated by the reduced mean distance from 4.4 A at A4 to 3.2 A at G8, is reproduced by the molecular mechanics calculation. These calculations provide insight into the underlying quantum chemical/structural origins of minor groove variations with sequence in DNA.

This combined structural biology approach using nuclear magnet resonance, biochemistry, and molecular modeling has shed unique insight into carcinogen adduct formation.

Similar cross-discipline combined studies will be necessary to investigate the role of sequence context and adduct stereoisomers in DNA repair and in gene regulation.

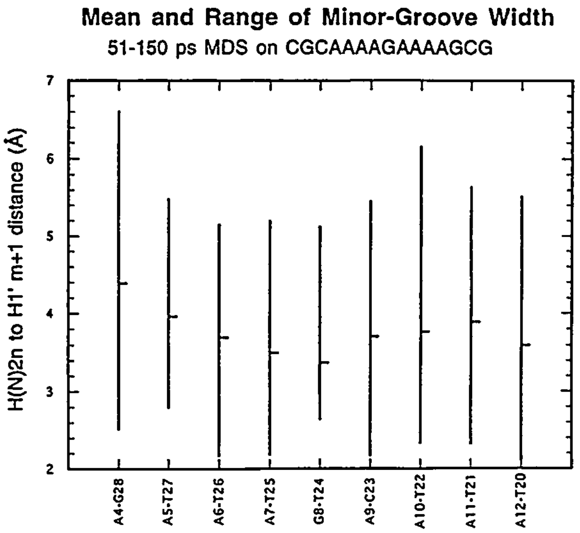

Figure 2. Molecular Dynamics Calculation of (n)-H(N)2 to (m+1)-H1' Distances in a Model DNA Sequence

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Novel Synthesis of Metal Cluster/Polymer Composite

Mira A. Josowicz (Materials Sciences)
Scott A. Chambers (Materials and Interfaces)

Project Description

The objective of this project was to develop an understanding of the mechanism of spontaneous, in situ formation of metal clusters and their density distribution in electroactive polymers. The unique properties of these materials were investigated in the context of the polymer-inorganic interfaces and charge-transfer reactions which play a fundamental role in a wide range of applications.

The functionalization of organic polymers with metal species is complex both in synthesis and in understanding the basic charge-transfer interactions. Considerable progress has been made in developing a molecular-level understanding of the chemical reactivity of the novel materials. The progress results from experimental effort which concentrated on synthesis, optical, spectroscopic, and electrochemical characterization of differently prepared polymer-metal cluster composite materials.

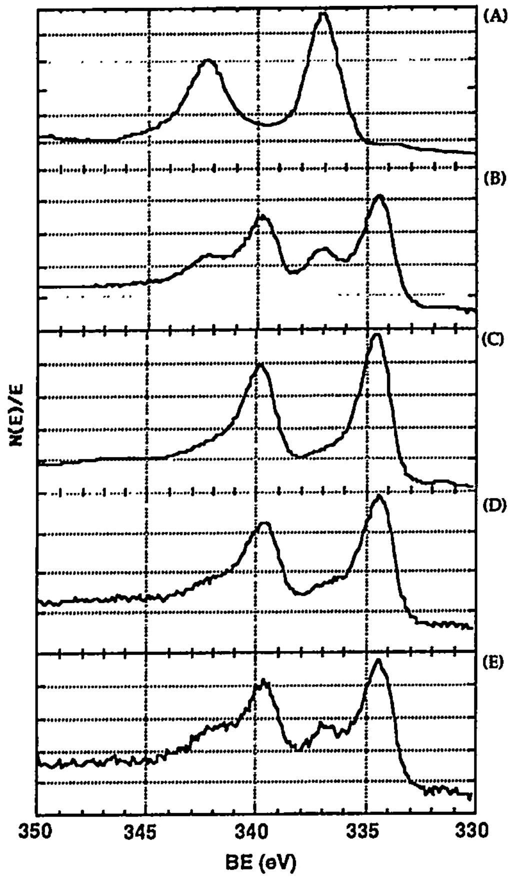
Technical Accomplishments

In the past year a detailed study was conducted on a polyaniline-palladium, PANi-Pd, system. The aspect of the synthesis of the nanomolecular composite materials was elaborated through a comparative study of one- or two-step processes. Hereby, the synthesis was carried out always electrochemically on platinum electrodes from electrolytes of similar composition. In the one-step process, the electropolymerization of aniline was carried out in the presence of Pd^{2+}. In the two-step process, firstly the PANi film was deposited and then one of the two possible preparation routes was applied: 1) PANi film was potentiostatically cycled within +0.5 and -0.3V for 10 minutes with 50 mV/s or a cathodic potential step from open cell potential (+0.5 V) to -0.25V was applied for one minute, 2) chemical relaxation of the freshly deposited PANi film in its oxidize (+0.75 V) or reduce state (-0.1 V) in solution containing Pd^{2+} was taking place. (All potentials are referred to the Standard Saturated Calomel Electrode, SSCE).

The dynamic nature of the relevant electrochemical and chemical preparation procedures resulted in different distribution and different binding-energy of the palladium species in the novel PANi-Pd thin films. That information was obtained from x-ray photoelectron spectroscopy analysis. The PANi-Pd films that were prepared in the two-step process by applying route 2 exhibit at least two oxidation states. The two Pd states can be distinguished in these x-ray photoelectron spectroscopy spectra by two bands: 1) Pd 3d5/2 of metallic Pd, which corresponds to the peak at 335.3 eV (also the peak at 339.5 eV corresponds to the Pd 3d3/2 of metallic Pd and 2) Pd 3d5/2 of Pd^{2+}, which corresponds to the peak at 337.8 eV (also the peak at 342.5 eV corresponds to the Pd 3d3/2 of Pd2+). In the case of chemical relaxation where the final applied polymerization potential for the PANi film was +0.75 V, only Pd^{2+} species can be seen (figure [A]). However, for the PANi-Pd sample, which was prepared on PANi film when the polymerization potential was stopped at -0.10 V, the peak corresponding to Pd^0 (at 339.5 eV) becomes prominent (figure [B]). The metallic state of the Pd cluster indicates that the electrons during the relaxation process have been withdrawn from the PANi matrix. However, for PANi-Pd samples prepared by the one-step procedure (co-deposition) the same result has not been obtained. The peak corresponding to Pd^0 is always more dominant in the spectrum (see figure [D] and [E]), indicating that a stable metallic Pd is formed, which is independent of the final stopping potential. The sample prepared by the cathodic potential step represents a small shoulder for Pd^{2+} and an intensive peak for Pd^0 (see figure [C]), showing that a stable metallic Pd layer can be formed by cathodic pulse technique.

The spatial distribution of the Pd species in PANi films according to the Auger electron spectroscopy and the depth profile analysis was found to be localized at specific regions of the PANi-film (surface, polymer/electrode interface, or within the bulk) depending on the preparation process. Discernible morphological differences between the PANi-Pd films were observed by optical microscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM). From the transmission electron microscopy and atomic force microscopy results, the Pd cluster was estimated to be approximately 100 nm. The cluster density distribution within the PANi film is driven by Fick's diffusion process. That information was obtained from electrochemical experiments. Furthermore, the electrochemical experiments also provided information about the absorption and desorption of hydrogen, as well as the hydrogen evolution. The processes have been found to be different from that occurring on a solid palladium metal electrode.

In addition to these studies, we have tested the PANi-Pd layers for hydrogen response by measuring the work function difference using the Kelvin Probe technique. The



X-ray photoelectron spectroscopy spectra of Pd 3d on PANi-Pd composite thin films prepared by: (A) chemical relaxation, (B) chemical relaxation, (C) by cathodic potential step, (D) one-step process with a potential stopped at 0.75 V, and (E) one-step process with a potential stopped at -0.1 V.

most sensitive response over a dynamic range of 10 to 10,000 ppm was achieved for the PANi-Pd layer with the metallic cluster as shown in the figure (C). The changes in the work function suggest that this film behaves as an electron acceptor and the hydrogen as an electron donor. The response is significantly influenced by the volume density of the Pd clusters in the PANi film.

Summarizing, it can be stated that the novel synthesis route for incorporation of metal clusters is promising for preparation of materials with interesting physicochemical properties. The recent progress in describing the fundamental properties of the nanocomposite materials provides a good basis for further investigation of other polymer-metal nanocomposite systems.

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M. Josowicz. 1994. "Application of Conducting Polymers in Electroanalysis." Presented at the Analytical Division Royal Society of Chemistry, University of Wales College of Cardiff, United Kingdom.

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Numerical Solution of the Schroedinger Equation

Robert J. Harrison (Theory, Modeling, and Simulation)

Project Description

We are working toward a fully numerical representation for one- and two-particle approximations to the solution of the many-electron Schroedinger equation. These efforts attempt to eliminate the major source of error in conventional calculations (the one-particle basis set) by adopting a well-defined numerical representation. The numerical approach is also expected to improve the scaling of the computational expense with respect to both system size and accuracy of the computation and improve efficiency on large parallel computers.

Mainstream ab initio methods for computing the electronic structure of molecules adopt the algebraic approximation by using basis sets at all levels of theory to turn the numerical problem of solving Schroedinger's equation into a large, sparse, eigenvalue problem. At the lowest level of theory, molecular orbitals (MOs) are expanded in a finite one-particle basis set, usually chosen as atomic centered orbitals (AOs). The underlying one-particle basis has recently emerged as the main source of error in conventional ab initio calculations. This increased understanding has come as a result of large full configuration interaction calculations, which provide the exact solution within a given one-particle basis set, and by more systematic design and study of basis sets. Yet more recently, it has become apparent that the algebraic approximation leads to inferior scaling of computational expense with respect to both required accuracy and system size, when compared to possible numerical alternatives.

Technical Accomplishments

Our interdisciplinary approach to numerical solution of the electronic Schroedinger equation leverages off work on adaptive finite-element methods (FEM) and in particular variations on multi-grid solution schemes. Initial work has focused on one-particle theories self-consistent field (SCF) which require only three-dimensional numerical functions. The key three-dimensional kernel is solution of Poisson's equation. Solution of the one-particle equation is necessary for solution of the two-particle equation which is of greater interest, from both a computational perspective and because a fully numerical two-particle function is of greatest potential utility. Figure 1 depicts a projection onto two dimensions of an adaptive three-dimensional mesh around a single model atom. Adaption within finite-element methods is essential for accurate treatment of the various length-scales present in molecular functions (i.e., peaks at the nuclei and exponential tails).

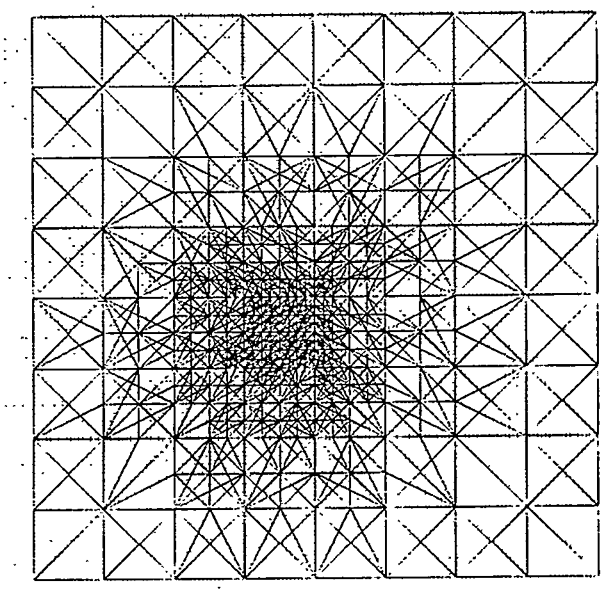


Figure 1. Projection onto Two Dimensions of an Adaptive Three-Dimensional Mesh Around a Single Model Atom

It will also be essential in describing the pair-function since in this context adaptation serves to reduce the effective dimension of the function. A graduate student from University of North Dakota has been working with us to solve, using finite-element methods, the self-consistent field and Möller-Plesset perturbation theory equations for two-electron atoms. His atomic self-consistent field program is now working with a non-uniform mesh. This work in high symmetry systems provides us with additional experience with applying finite-element methods to chemical systems with no symmetry and gives us access to exact solutions for comparison purposes and for the analysis of asymptotic behavior and numerical approximations.

In addition to finite-element methods, we are also investigating wavelets as a secondary approach to the numerical representation. Wavelets provide an inherently multi-level approach to the representation (or compression) of numerical information and the fast solution of differential equations. Most importantly they form an orthogonal basis with sparse representations of many operators in both the real and frequency domains. Figure 2 illustrates the sparsity present in the wavelet representation of the Green's function for the one-dimension Poisson equation—there are only O(N) non-zero elements.

We have the corresponding operators for two and three dimensions. This work is much more speculative since there has been limited application of these methods beyond two dimensions. However, any results will be of great interest.

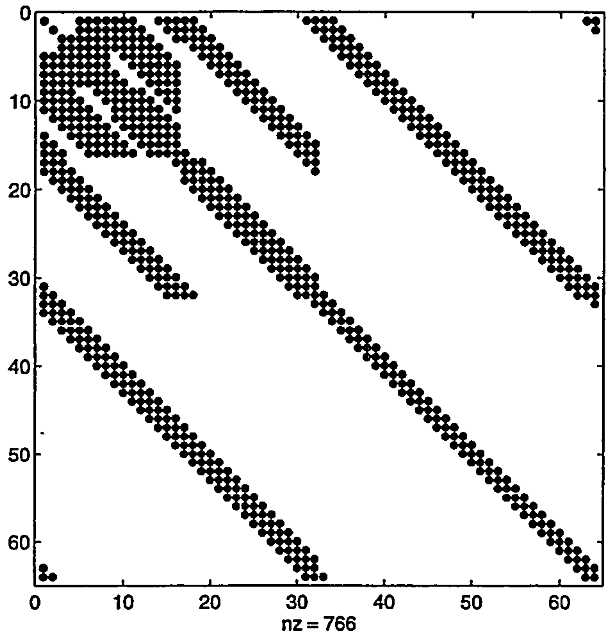


Figure 2. The Sparsity Present in the Wavelet Representation of the Green's Function for the One-Dimension Poisson Equation

PBPK-Based Breath Analysis Instrumentation Demonstration

Karla D. Thrall (Health Protection)

Project Description

Research will be directed toward 1) the development and validation of physiologically based pharmacokinetic (PBPK) models to describe the uptake, distribution, metabolism, and excretion of toxic chemicals in experimental animals; 2) integration of mechanistic information to provide a scientifically based means of extrapolating animal PBPK models to apply to humans; and 3) technological improvements on a sensitive new breath-analysis system that has real-time appraisal capabilities. The long-term goal of this research is to produce a portable, or semiportable, real-time monitoring instrument capable of characterizing human tissue levels of volatile chemicals in waste site cleanup workers at Hanford and elsewhere in the DOE complex.

Technical Accomplishments

Breath-Analysis Instrumentation

The feasibility of developing the PBPK-Based Breath-Analysis instrument for field use pivots on technological breakthroughs that have enabled laboratory-bound mass spectrometer instrumentation to become "field portable." The combination of a new, small, lightweight mass spectrometer and a breath analyzer now makes it possible to monitor workers for exposure to hazardous materials in the field. The breath analyzer links a subject's exhaled breath with the mass spectrometer for a continuous analysis of specific gases: readings can be generated every 1.5 seconds.

In FY 1994, the human breath-inlet device was remodeled for use with laboratory rats. The remodification provided a revolutionary toxicological research tool to aid in the understanding of biokinetics and, thus in the refinement and validation of PBPK models. To demonstrate this, a series of animal experiments were conducted.

In the first set of experiments, animals were restrained in restraint tubes, and connected to a mass spectrometer via the rat breath-inlet device such that their exhaled breath was directly linked with the TAGA mass spectrometer located at PNL. Background, or baseline, data was collected for several minutes, then each animal received a single intravenous injection of carbon tetrachloride via an indwelling jugular vein cannula (0.6 mg/kg body weight). Immediately upon injection, it was possible to monitor carbon tetrachloride in the exhaled rat breath using the breath-analysis instrumentation (Figure 1).

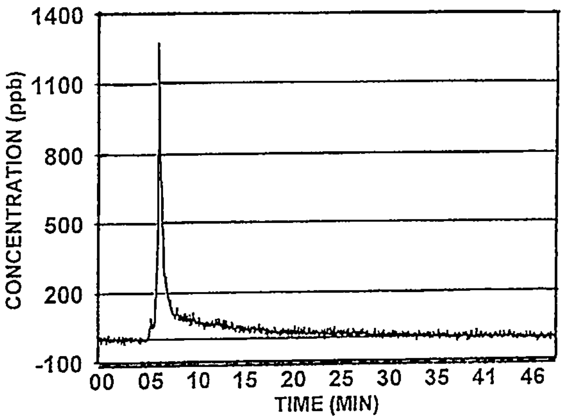


Figure 1. Real-time measurement of the combined exhalation of CCl_4 from two rats receiving a single intravenous injection (250 μL CCl_4 in isotonic saline, 0.6 mg/kg BW).

In the second set of experiments, animals were restrained as before, and baseline data was collected for several minutes. The animals were then removed from the inlet device, given a single oral dose of carbon tetrachloride in a corn oil vehicle (doses ranging from 25 to 100 mg/kg body weight), and then reconnected to the inlet to monitor the real-time exhalation of carbon tetrachloride, a carbon tetrachloride metabolite (chloroform), and biomarkers of lipid peroxidation (i.e., toxicity) - ethane, pentane, and acetone (Figure 2).

PBPK Modeling

The primary goal of this project during FY 1994 was to design a series of laboratory tests at PNL to demonstrate the capabilities of a system that combines sensitive new breath-analysis instrumentation with PBPK models using carbon tetrachloride as the example chemical.

Previous developmental efforts on a carbon tetrachloride PBPK model served as the foundation to produce a model that can successfully predict the kinetics of exhaled breath levels of carbon tetrachloride in laboratory rats following either an intravenous or oral exposure. This is illustrated in Figures 3 and 4.

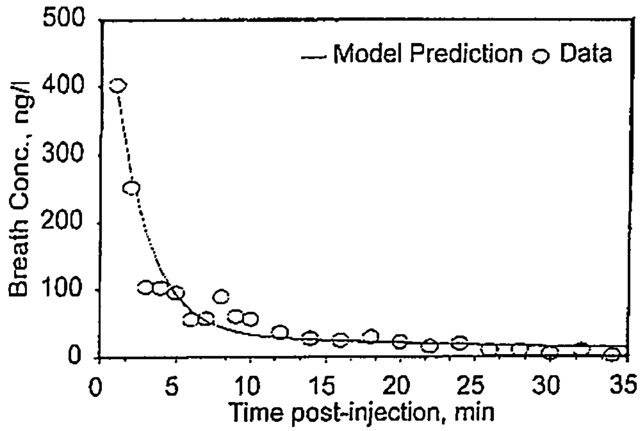


Figure 2. Comparison of the experimental data from Figure 1 with the model prediction using the PBPK model described in the text.

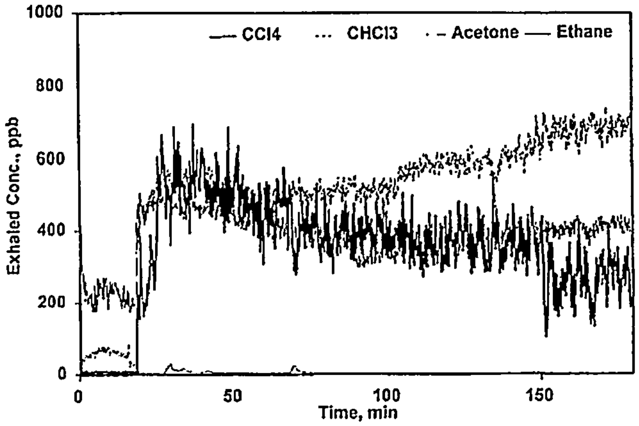


Figure 3. Real-time measurement of the combined exhalation of CCl_4 chloroform ($CHCl_3$), ethane, and acetone from four rats each receiving an oral gavage dose of CCl_4 (25 mg/kg in corn oil vehicle).

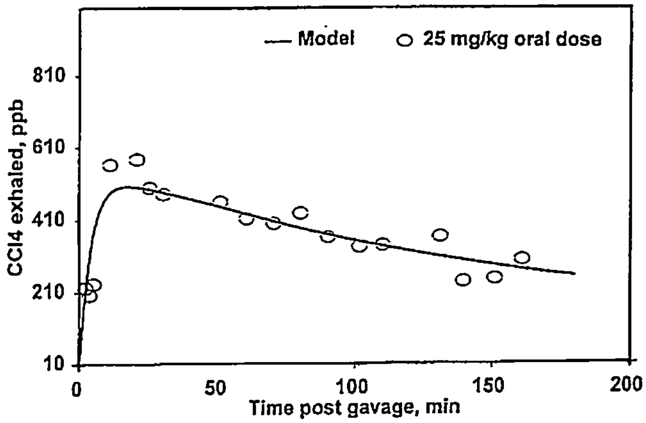


Figure 4. Comparison of the CCl_4 experimental data from Figure 3 with the model prediction using the PBPK model described in the text.

As a direct result of these experiments, a series of additional studies have been planned to further enhance the general scientific understanding of carbon tetrachloride biokinetics.

Toxicokinetics

Toxicokinetic studies are needed to develop the data to characterize the kinetics of chemical distribution and to describe the metabolic fate of chemicals. To fully validate the PBPK model for carbon tetrachloride tissue distribution, it is vital to measure not only the exhalation of the parent and metabolites, but also the concentration in the transfer compartment (blood).

During FY 1993, a method was developed for the measurement of carbon tetrachloride in blood using gas chromatography with electron capture. In FY 1994, this method was used to analyze the concentration of carbon tetrachloride in animals given an intravenous injection of carbon tetrachloride. During the course of these experiments, a problem was discovered which points doubt at both the blood collection and analytical procedure. These studies continue into FY 1995.

Publication

K. D. Thrall and D. V. Kenny. 1994. "Validation of a physiologically based pharmacokinetic model by monitoring carbon tetrachloride in real-time in the expired breath of the rat." *Toxicol. Appl. Pharmacol.* (submitted).

Presentations

K. D. Thrall, G. W. Endres, and D. V. Kenny. 1994. "Instrumentation to improve worker health protection." Presented at the DOE Occupational Safety and Health Conference, San Diego, California, October 25-28.

K. D. Thrall and D. V. Kenny. 1994. "Real-time breath-analysis instrumentation and physiologically based pharmacokinetic modeling: A new opportunity in chemical mixtures research." Presented at the EPA/HERL *Chemical Mixtures and Quantitative Risk Assessment* symposium, Research Triangle Park, North Carolina, November 7-10.

K. D. Thrall and D. V. Kenny. "Validation of a carbon tetrachloride PBPK model using real-time kinetic data." To be presented at the 1995 Annual Meeting of the Society of Toxicology, Baltimore, Maryland, March 5-9, 1995.

Other Accomplishments

Partially supported a DOE Science and Engineering Research Semester (SERs) student.

Physiologically Based Pharmacokinetic Modeling of Organic Waste-Site Chemicals

Karla D. Thrall (Health Protection)

Project Description

The goal of this research was to coordinate with on-going physiologically based pharmacokinetic (PBPK) model development efforts and to enhance PNL's technical expertise is PBPK modeling. In particular, PBPK models were developed to characterize the human tissue uptake and retention of volatile organic chemicals that pose a potential health concern to hazardous waste cleanup workers.

Occupational exposure to volatile organic compounds have traditionally been monitored by measurements of airborne concentrations. However, although this methodology documents that exposure has occurred, it does not tell us anything about the internal chemical dose to the critical target organ. Thus, calculation of potential adverse health risk is difficult. A challenge faced by toxicologists and industrial hygienists alike, it to identify and monitor biological changes, or biomarkers, induced by exposure to toxicants, and thus determine the internal dose following exposure. The development of a PBPK model provides a powerful tool for understanding and predicting the fate of hazardous chemicals in the body. A PBPK model can provide the scientific link between actual chemical exposure and observable adverse health effects by quantitatively portraying the disposition of a chemical and its metabolism from the time it is absorbed to the interaction with various body tissues.

Technical Accomplishments

The focus of this project was directed toward the acquisition of tools to improve our capabilities in PBPK modeling. To that end, much of the effort under this project was to upgrade our current version of SimuSolv (Dow Chemical Company, Inc., Midland, Michigan). SimuSolv is considered the state of the art in simulation and optimization software. The software has the ability to provide a continuous simultaneous simulation of the set of differential equations as might describe chemical uptake, distribution, metabolism, and elimination in a PBPK model.

The previous version of SimuSolv was on a Sun Sparc Model 10-41 workstation platform with a single-user FORTRAN compiler. The single-user FORTRAN compiler was leading to a serious reduction in modeling productivity, because only one user at a time could compile a PBPK model. The upgrade of SimuSolv to an HP9000 workstation with a multiple-user FORTRAN compiler greatly enhanced the modeling efforts by reducing the time required to wait for the workstation FORTRAN system to recognize an additional user.

Protein Structure Analysis

Richard J. Douthart (Biology and Chemistry)
Keith Dunker and Robert Miller (Washington State University)

Project Description

A critical "Grand Challenge" problem in structural biology is the reasonable prediction of protein secondary and tertiary structure from primary sequence. The current emphasis on mapping and sequencing entire genomes is rapidly producing derived protein sequence at an ever increasing rate. To be useful, this information must be transformed into reasonable protein structures from which function can be inferred.

Previously, collaborative work with Washington State University centered on the elusive secondary structure prediction problem. Working then with graduate student who is now a staff member at PNL, the "structural attributes" method for comparing secondary structure prediction schemes was developed. This method although not a structural prediction scheme itself has been used widely in evaluating existing schemes. Interestingly, structural attribute studies have not as yet yielded a set of best attributes that when linearly combined lead to significantly better predictive scores.

Technical Accomplishments

The initial emphasis of the project was to attempt to get more meaningful attribute descriptors by concentrating on the geometry of folded polypeptides. Initial efforts dealt with partitioning the space of Psi and Phi, the dihedral angles of the peptide bond, by applying a classical min-max clustering algorithm. Unusual local clustering was obtained that hinted at new and subtle types of transition secondary structure. From these results, a conformer alphabet was developed applying the alphabet to the predominately alpha protein deoxy erythrocruorin, the beta protein actinoxanthin, and the mixed protein ribonuclease A, rich repeating patterns of putative secondary structure were obtained. Our results indicate that besides the acknowledged effects of long-range interactions, the attempts at strict definition of regions in terms of few classical structure types also contributes errors in overall structure prediction.

The use of neural networks and genetic algorithms was explored during the second year of this project with some initial interesting folding results, especially in strong alpha regions. Our results strongly indicate that region membership into defined secondary structure classes is fuzzy and that application of fuzzy logic and algorithms to the structure and folding problem would be very beneficial.

Publications

R. T. Miller, R. J. Douthart, and A. K. Dunker. 1994. "Identifying Repeated Structural Elements in Proteins." In *Proceedings of the Twenty-Seventh Hawaii Conference on System Science*.

R. T. Miller, R. J. Douthart, and A. K. Dunker. 1994. "A Three-Dimensional Description of Amino Acid Environments in Protein." In *Procedures in Protein Chemistry* (in press).

Presentation

R. T. Miller, R. J. Douthart, and A. K. Dunker. 1994. "Identifying Repeated Structural Elements in Proteins." Twenty-Seventh Hawaii Conference on System Science. Maui, Hawaii.

Semipermeable Membrane Devices for Sampling Nonpolar Organic Compounds in Air, Water and Soil

Eric A. Crecelius and Lisa F. Lefkovitz (Marine Sciences Laboratory)

Project Description

Semipermeable membrane devices (SPMDs) have the potential for use as passive samplers in both the environment and in waste systems. SPMDs have the ability to passively concentrate hydrophobic organic chemicals (HOCs) from air and water, thus providing a time-integrated sampler for chemicals that may be below detectable levels by conventional sampling techniques. The selectivity and concentration factor depend upon the chemical, the type of membrane, and the type of material inside the membrane.

The purpose of this study was to demonstrate the application of SPMDs for monitoring contaminants in air, water, soil, and sediment in the environment. In addition, the SPMD was used as a surrogate for estimating bioaccumulation of chemicals in organisms.

Technical Accomplishments

We have been actively investigating the use of these devices for predicting bioaccumulation of nonpolar organic compounds by aquatic organisms (e.g., clams) from contaminated aquatic environments and have had very promising results. A number of studies were completed during FY 1994. In addition, several clients, including NOAA and some environmental consulting firms, have requested SMPDs and we have worked with them to deploy the devices at various sites including locations off the coast of Alaska and in the Spokane River.

A brief description of some of the studies that we performed in the last year follow:

The uptake of pyrene, a polynuclear aromatic hydrocarbon (PAH) compound, was measured into SPMDs in conjunction with an oyster bioaccumulation test. The purpose of this task was to demonstrate the correlation between the concentration factor for SPMDs and the bioaccumulation factor for oysters under controlled conditions in the laboratory. All samples have been collected and extraction and analyses are in progress. We anticipate using these data for either presentation and/or publication.

A field survey was conducted with both SPMDs filled with lipid and with polyethylene film samples in Elliot Bay, near Seattle, to demonstrate the application of this device for identifying sources and transport of chemicals in natural waters. Preliminary results of the polyethylene sheets show a definite trend in levels of contaminants near the Duwamish River, which is a source of contamination to Puget Sound. SPMD and polyethylene film results will also be compared to mussel tissue concentrations collected at corresponding locations.

A laboratory study was performed to assess the uptake rates of various nonpolar organics, including polychlorinated biphenyls (PCBs), pesticides, and PAHs from two contaminated sediments. Both polyethylene sheets and SPMDs filled with lipid were placed in contact with a sediment water slurry and rolled for a period of up to 2 months. Bags and poly sheets were removed at regular intervals over this period and the rate of release from the sediments and the subsequent uptake by the SPMDs and poly sheets were evaluated. Equilibrium appeared to be reached more quickly in the poly sheets. For some of the larger PAH compounds, equilibrium did not appear to be achieved even after 60 days. This makes comparison to actual tissue bioaccumulation results questionable, as the standard bioaccumulation tests only last 28 days. Uptake into the SPMDs and poly sheets will be compared to actual bioaccumulation results associated with previous tests performed on these sediments.

Presentations

L. F. Lefkovitz and E. A. Crecelius. "Use of Semipermeable Membrane Devices (SPMDs) to Monitor PAHs in Elliot Bay." To be presented at the Puget Sound Research, '95, Bellevue, Washington.

L. F. Lefkovitz, E. A. Crecelius, and T. J. Gilfoil. 1994. "The Use of Semipermeable Membrane Devices to Predict Bioaccumulation of Hydrophobic Organic Contaminants." Presented at the Society of Environmental Toxicology and Chemistry, 15th Annual Meeting, Denver, Colorado.

Site Specific DNA Damage by Radiation and Chemicals

Brian D. Thrall and David L. Springer (Biology and Chemistry)
Michael A. Kennedy (Macromolecular Structure and Dynamics)

Project Description

Exposure of cells to radiation and chemicals results in DNA damage which may ultimately be expressed as an adverse health effect. The objective of this project was to develop model systems in which studies of the functional consequences of DNA damage can be directly linked to the structure of the DNA damage in a site-specific and homogenous manner. These efforts include not only synthesis and purification of DNA containing a single and site-specific DNA adduct, but development of model systems of DNA repair and replication which can measure the functional consequences of the adduct.

Technical Accomplishments

Many carcinogens are metabolically activated and can result in multiple types of adducts which, although chemically identical, differ stereochemically and structurally. Since the ability of cells to repair and replicate damaged DNA could depend dramatically on the structure of the damaged DNA, it is difficult to determine which type of adduct(s) is important to the ultimate health effect. During FY 1993 we synthesized, modified, and purified oligonucleotides bearing a single and site-specific adduct from benzo[a]pyrene diol epoxide (BPDE). We are studying the structural basis for sequence-specific adduction of DNA by BPDE. We have found that in sequences which are poorly adducted by BPDE, the minor groove is narrowed. Since the predominant mode of covalent binding by BPDE is through the minor groove, these findings may in part explain the structural basis for sequence-specific binding of DNA by BPDE. In addition, these findings may have important implications to the specificity of mutagenesis in chemically induced tumors.

During FY 1994, efforts were focused on developing model systems which are useful for studying the repair of DNA damage. We have found that nuclear extracts from human cells contain the enzymatic activity necessary for repair of plasmid DNA bearing BPDE adducts. Plasmids damaged with BPDE were incubated with nuclear extracts in the presence of ATP, deoxynucleotide triphosphates, and digoxigenin-labeled deoxyuridine triphosphate. After incubation, the DNA was linearized by restriction digestion, separated by gel electrophoresis, and the incorporation of labeled nucleotide was measured by chemiluminescence and autoradiography. We have shown that "repair synthesis" is significantly greater in plasmids damaged with BPDE than in nonadducted DNA (Figure 1).

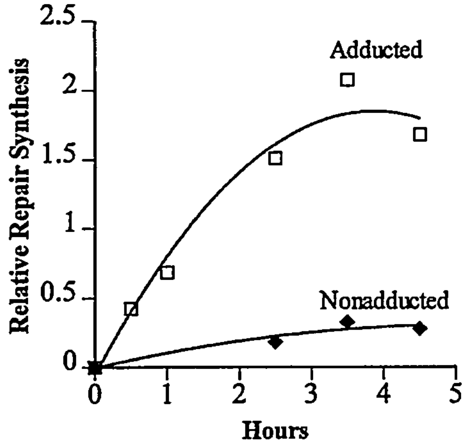


Figure 1. Time Course of Repair Synthesis in Nonadducted and BPDE-Adducted DNA

Furthermore, the level of repair synthesis is linearly related to the level of DNA damage as would also be expected if the extract contains bona fide DNA repair activity (not shown). We have also demonstrated that the majority of the repair synthesis activity is due to DNA polymerase α or δ, but not ß. Aphidicolin, which inhibits polymerase α and δ, but not ß, eliminated approximately over 80% of the repair synthesis (Figure 2). Therefore, excision repair of BPDE adducts in our system does not appear to significantly involve polymerase ß. However, we cannot as yet distinguish between polymerase α and δ using aphidicolin as an inhibitor.

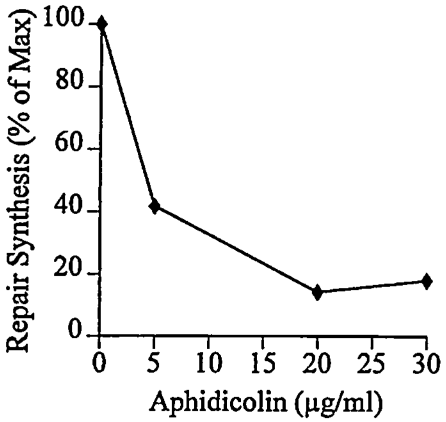


Figure 2. Effect of Aphidicolin on Repair Synthesis

We have also found that labeled nucleotide is incorporated during repair synthesis by nuclear extracts into form I (supercoiled) plasmid, suggesting that the extract contains both ligase and topoisomerase activity. This has led us to pursue experiments to determine whether topoisomerase activity is involved in DNA repair. Topoisomerase I (topo I) introduces single-strand breaks and thereby relaxes supercoiled DNA. Topoisomerase II (topo II) introduces double-strand breaks in an ATP-dependent reaction, and has gyrase (supercoiling) activity.

Novobiocin, a selective inhibitor of topoisomerase II, caused a concentration-dependent inhibition of repair synthesis. At concentrations of 1 mM novobiocin, repair synthesis was reduced nearly to control levels. In addition, addition of bacterial topo I inhibited repair synthesis by approximately 50%. We interpret these results to indicate that topoisomerase activity indeed influences DNA repair synthesis. Also, since both the inhibition of gyrase (topo II) activity and the addition of relaxing (topo I) activity resulted in decreased repair synthesis, it may be that the supercoiled structure of DNA is important in efficient DNA repair. These findings have significant implications since topoisomerase activity is known to be involved in many other cellular processes including cellular division, apoptosis, and gene expression.

The use of in vitro repair assays to measure repair of damaged plasmids has enhanced our ability to determine the role of cellular enzymes in DNA repair without the influence of confounding factors such as cytotoxicity. We are currently using this approach to further elucidate the role of topoisomerases in DNA repair, as well as to determine the role of DNA structure in the repair of DNA damage.

Publications

B. D. Thrall. 1994. "Repair of benzo[a]pyrene diol epoxide-modified DNA by human nuclear extracts." In *Proceedings of the 11th Annual Pacific Northwest Association of Toxicologist Annual Meeting*, Newport, Oregon, October 7-8.

B. D. Thrall, D. L. Springer, and M. A. Kennedy. 1994. "Structural studies of sequence-specific benzo[a]pyrene diol epoxide adduct formation." In *Proceedings of the Environmental Mutagenesis Society Annual Meeting*, Portland, Oregon, May 7-12. In *Environ. Mol. Mutagenesis* 23(suppl 23):65.

B. D. Thrall, A. J. Kube, and D. L. Springer. "*In vitro* repair of benzo[a]pyrene diol epoxide adducted DNA in reconstituted nucleosomes." *Biochemistry* (in preparation).

Presentation

M. A. Kennedy, D. L. Springer, and B. D. Thrall. 1994. "Structural studies of sequence-specific benzo[a]pyrene diol epoxide adduct formation." Gordon Conference on Magnetic Resonance in Medicine and Biology, Henniker, New Hampshire, July 17-22.

Other Accomplishments

Collaborations with Dr. Michael Smerdon, Washington State University, Department of Biochemistry and Biophysics, were established through this project.

Solid Waste Material Flow Modeling

Gregory M. Holter (Systems Engineering and Project Engineering)

Project Description

Solid wastes are inevitable byproducts of human activities. As an example, 180 million tons of garbage and 11 billion tons of industrial waste are disposed of in the U.S. each year; other countries also face increasingly significant solid waste problems. Every segment of our society (individual, household, corporation, community, state, region, nation) is involved in the generation of this waste, and therefore the activities generating the wastes and the resulting waste compositions are very diverse. These diverse waste products represent a complex threat to the environment but, at the same time present opportunities to recover usable materials and/or energy from them.

The diversity and complexity of the solid waste problem has not been adequately addressed in our society, resulting in the lack of a coherent, integrated approach to the solution of present waste problems and/or prevention of future ones. Approaches to waste management, waste minimization, and waste regulation have been responsive (or reactive) to particular problems, and compartmentalized to match the specific responsibilities of the particular groups involved. This project provides a mechanism for combining technical, economic, sociological, and legal solutions to this complex situation in a synergistic and compatible manner. The resulting approach will provide a systems perspective on the solid waste problem and on possible solutions to it, to help identify and evaluate viable long-term strategies for the management of the various types of solid waste.

The primary objective of this project was to evaluate solid waste practices that might have negative implications on the global environment and develop recommendations for reducing such impacts. A study was performed, based primarily on literature review but also including input from brainstorming sessions among PNL staff, to identify and categorize such impacts.

The scope of the study included the range of nonhazardous solid wastes, including municipal solid waste, industrial solid waste, and industry-specific wastes from activities such as construction, demolition, and land-clearing. In general, hazardous wastes were not included in the study; however, a discussion of moderate risk wastes was included.

Technical Accomplishments

The study concluded that several different types of impacts can result from solid waste practices:

- direct impacts resulting from the amounts of wastes produced, managed, and disposed
- direct impacts resulting from constituents in the wastes
- indirect impacts (e.g., waste of materials or other resources) relating to solid waste practices.

The study also concluded that there are different levels of severity associated with these impacts. The study found that, although development of the best available technologies and practices in industrialized countries has drastically reduced impacts relating to solid waste, potential areas of concern remain for industrialized countries. The more serious concern, however, is prevention and mitigation of environmental impacts from solid waste practices in less-developed countries and industrializing nations.

Also during FY 1994 the prototype Macro Material Flow Model previously initiated was completed, and demonstrations of the prototype were held with several organizations involved in solid waste management to obtain their feedback. The prototype simulates major portions of the Macro Material Flow Model functionality, and provides a basis for presenting and refining the model concept, confirming the operability of the model and the usefulness of the results, and facilitating liaison activities with prospective clients. The Macro Materials Flow Modeling concept and approach provide a total-system-oriented basis for evaluating potential impacts from various solid waste management system configurations and operating scenarios.

Publications

M. M. Davis, G. M. Holter, T. J. DeForest, D. C. Stapp, and J. C. DiBari. 1994. *Possible Global Environmental Impacts of Solid Waste Practices*, PNL-10149, Pacific Northwest Laboratory, Richland, Washington.

G. M. Holter, D. C. Stapp, and S. R. Shaver. 1994. "Application of Macro Material Flow Modeling to Regional Solid Waste Planning." 87th Annual Meeting of the Air & Waste Management Association, Cincinnati, Ohio. PNL-SA-23055, Pacific Northwest Laboratory, Richland, Washington.

Other Accomplishments

This project directly supported an AWU student during the summer of 1993 and a TRAC appointee during the summer of 1994.

A senior engineer was also hired in FY 1993 to work part-time on this project, because of his expertise and extensive business contacts within the solid waste area. His involvement continued during FY 1994.

Under this project, PNL also established a linkage with State University system of California. Dr. Samuel A. Vigil, a Professor in the Civil and Environmental Engineering Department of the San Luis Obispo campus of Cal Poly, was nominated and selected for an appointment within the recently announced PNL Affiliate Staff Scientist (PASS) program. Dr. Vigil has strong interest and considerable experience in the area of solid waste management, and will extend our capabilities in the modeling and analysis of solid waste management options.

Spectral Mapping of the V4 Band and Determination of the Molecular Constraints for the Chlorine Nitrate Molecule

Steven W. Sharpe (Chemical Structure and Dynamics)

Project Description

The goal of this project was to map and catalog the spectral positions of individual rovibrational transitions from the ground to the n_4 vibrational state of the chlorine nitrate molecule. These individual lines are assigned specific quantum values and used to calculate accurate molecular parameters associated with both the ground and upper vibrational states. This particular band is of interest because it lies in the 8 to 12 micron atmospheric window region. It is our ultimate intention to submit these findings for inclusion in the HITRAN spectral database.

Technical Accomplishments

Atmospheric ozone degradation proceeds via a catalytic process involving atomic chlorine. Chlorine nitrate has been postulated to act as a reservoir for atomic chlorine and may be important in removing chlorine from the atmosphere (Rowland et al. 1976; Hudson and Reed 1979). Fast and reliable techniques for the identification and quantification of $ClNO_3$ rely upon accurate spectral mapping of this species. In addition, a determination of the molecular rotational and vibrational constants can be used to predict the position of yet unseen transitions.

Atomic chlorine, produced by the photodissociation of freons (e.g., CF_2Cl_2) is known to be responsible for the catalytic decomposition of ozone in the stratosphere. Chlorine nitrate has been postulated to act as a reservoir for atomic chlorine and may be useful in terminating this catalytic cycle. These processes may be summarized as follows:

(1) $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$
(2) $O_3 + Cl \rightarrow ClO + O_2$
(3) $NO_2 + ClO + M \rightarrow ClONO_2 + M^\dagger$

Although there are a number of infrared spectra reported for $ClONO_2$ these are not of sufficiently high resolution and/or quality to allow for an unambiguous rovibrational assignment of the observed transitions. An infrared "road map" and accurate upper state molecular constants are needed for $ClONO_2$ and would greatly facilitate its characterization in the earth's atmosphere.

Earlier, high resolution spectroscopic studies of $ClNO_3$ had been thwarted by a number of technical problems including spectral congestion, extensive pressure broadening, and Doppler broadening (Chance and Traub 1982; Bell et al. 1992). By using recently developed technology, it will be possible to avoid these problems and obtain unambiguous, fully rotationally resolved spectra for $ClNO_3$ (Sharpe et al. 1990).

We report the results of our spectroscopic study of chlorine nitrate in the 12.8 micron (i.e., 780 cm^{-1}) region using apparatus and technology developed in the authors laboratory. The 12.8 micron region corresponds to the infrared active, n_4 vibrational mode of $ClNO_3$ and, consists of an out-of-plane bending motion.

Approach

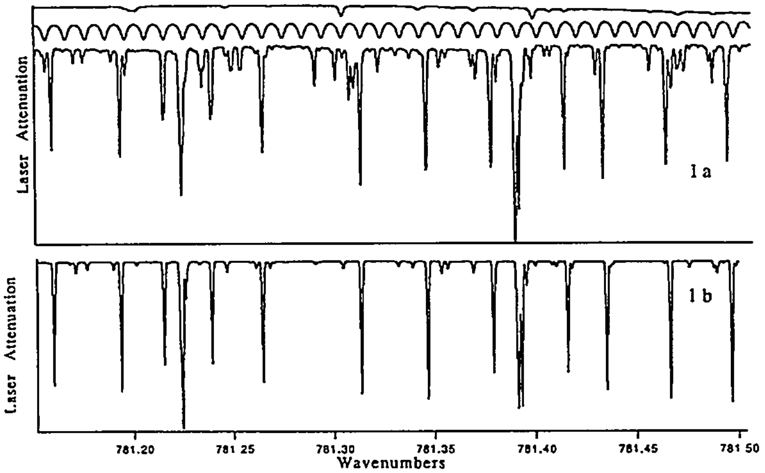
By producing ultra cold molecules in a collision free environment many of the problems that plague conventional spectroscopic techniques including spectral congestion, pressure broadening, and Doppler broadening can be avoided. In these experiments, a sample (e.g., 1% $ClONO_2$) is entrained in a carrier gas such as argon or helium and allowed to expand into a vacuum chamber. During the expansion, the entrained molecules are cooled adiabatically and typical rotational temperatures are 10K. The cold molecules are then probed using a diode laser technique pioneered by this author. The chlorine nitrate sample was synthesized in the laboratory of Professor Jean'ne Shreeve at the University of Idaho.

Basically, the expanding effluent from a slit nozzle undergoes rapid adiabatic cooling and focusing perpendicular to the axis of expansion. Rapid cooling of internal energy relieves spectral congestion by placing the entrained molecules into their lowest quantum states while focusing of the molecular beam removes much of the Doppler broadening inherent in standard spectroscopic techniques. Both of these effects work in concert to increase sensitivity, reduce spectral congestion and minimize Doppler broadening. Instrumental line widths on the order of 17 MHz (FWHM) may be realized with this approach.

Results

We have scanned over approximately 10 wavenumbers, capturing the entire n_4 band and part of the n_3 band at a rotational temperature of ~14K. A small section of the n_4 band is displayed in the figure. Both A- and B-type transitions are observed in the n_4 band and we have currently assigned over 280 transitions. Results of fitting these transitions to a Watson type distortable rotor model appears in the table. This analysis will continue as new transitions are assigned.

We are also attempting to derive estimates for absolute cross sections of individual transitions. This is done by expanding a known amount of NO_2 along with the $ClONO_2$ and noting the relative peak heights for each species. This combined with an estimate of $ClONO_2$ in the expansion will result in absolute cross sections.



Upper trace corresponds to experimental observation of chlorine nitrate in supersonic expansion. Lower trace corresponds to molecular simulation based on lower state constants in Suenram and Johnson (1977) and our upper state constants determined here.

Results of fitting these transitions to a Watson type distortable rotor model.

	Ground6	v4
A	0.403804	0.403939(4)
B	0.092631	0.09253(1)
C	0.075324	.0751367(9)
ω	0	780.01594(6)
ΔJK	.1218e-6	.1216e-6
ΔJ	.179e-7	.178e-7
ΔK	.3598e-6	.385e-6

All values are reported in cm^{-1}.

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Other Accomplishments

Development of novel supersonic beam source for generation of ultra cold molecular beams.

Pending cross-section analysis, these results will be submitted to HITRAN for archiving.

Spectroscopy Techniques for Analysis of DNA Damage

Alfred F. Fuciarelli (Biology and Chemistry)

Project Description

Exposure of DNA to free radical-generating agents, such as ionizing radiation and selected chemicals, results in a multiplicity of molecular damage that is also characterized in terms of the spatial distribution along the DNA molecule. We are using specific DNA products as molecular probes of nucleic acid damage in an effort to increase our understanding of the mechanisms underlying free radical damage to cells and the impact of these lesions on biochemical processes. Oligonucleotide synthesis techniques were used to prepare DNA substrates of defined base composition for irradiations, and mass spectrometry methodology was used for product analysis to assess 1) electron migration along DNA as a potential mechanism by which radiation-induced damage can be manifested distal to the sites of initial energy deposition in DNA, 2) the influence of DNA base sequence and DNA structure on the distribution of free radical-induced molecular products and, 3) the influence of the microenvironment on product distribution in irradiated solutions of DNA.

Technical Accomplishments

Electron migration along DNA is a mechanism by which radiation-induced damage can be manifested distal to the initial point of energy deposition in DNA and is an important contributing mechanism to formation of locally multiply damaged sites in DNA. In this project, we have made use of 5-bromouracil (5-BrU) as a molecular indicator of electron reactions in aqueous solutions of DNA exposed to ionizing radiation to study migration of damage along synthetic oligonucleotides. In earlier phases of this project, we found that 1) electron migration occurred in aqueous solutions of DNA and that differences in the extent of migration occurred as a function of DNA conformation and base sequence, 2) electrons were capable of migrating up to seven base pairs in a segment of DNA containing guanine bases, 3) electrons were capable of preferential migration from the 5' to 3' direction which is attributed to greater overlap of the pi electron clouds in adjacent DNA bases. In FY 1994, we examined the mechanism underlying electron interactions with 5-BrU and sought to experimentally verify sources of hydrogen atoms which are captured by the intermediary uracilyl radical. These studies have important implications with regards to interpretation of experiments involving electron migration and radiation-induced formation of DNA strand breaks.

In solutions exposed to ionizing radiation solvated electrons (e_{aq}^-), formed during water radiolysis, participate in a dissociative electron attachment reaction with 5-BrU leading to the formation of bromide ions and uracil-5-yl radicals. The uracil-5-yl radicals formed during radiolysis are capable of abstracting hydrogen atoms from other sources in solution ultimately leading to the formation of uracil. For example, in solutions of 5-BrU exposed to ionizing radiation, t-butanol was found to be a source of hydrogen atoms. However, in molecular models of B-form DNA containing 5-BrU, the bromine atom is found to be in van der Waals contact with the deoxyribose sugar in the same strand on the 5' side of the 5-BrU moiety. This intimate contact has led to the hypothesis that hydrogen atom abstraction by the uracil-5-yl radical could potentially occur from the C(2') position of the adjacent deoxyribose on the 5' side of the 5-BrU moiety in DNA.

Understanding the early events underlying 5-BrU destruction is important for gaining insight into the subsequent events that result in radiation-induced DNA strand breaks and enhanced cellular radiosensitivity. In this study, we used deuterium oxide and 2-methyl-2-propanol-d_{10} (deuterated t-butanol) to identify the source of the captured hydrogen atom in irradiated solutions of 5-BrU, a dinucleotide containing 5-BrU on either side of a base capable of transferring electrons, a single-stranded oligonucleotide, and a double-stranded oligonucleotide.

The interaction of 5-BrU with solvated electrons produced by exposure to ionizing radiation leads to formation of uracil-5-yl radicals which are capable of abstracting hydrogen atoms from other chemical species to form stable uracil. The results of this work suggest that the local environment of the uracil-5-yl radical is a key factor in the determination of the source of the hydrogen atom. If the uracil-5-yl radical is formed as an unbound species in solution (i.e., from destruction of a free 5-BrU base), then the abstracted hydrogen atom is obtained predominantly from a solute hydrogen atom donor species such as t-butanol. This mechanism follows from our data showing the quantitative formation of 5-deuterouracil in solutions containing deuterated t-butanol. On the other hand, a uracil-5-yl radical which finds itself incorporated in a single- or double-stranded oligonucleotide is most likely to abstract a hydrogen atom from another moiety also contained in the oligonucleotide. This mechanism is consistent with our data showing that a predominance of non-deuterated uracil is found in 5-BrU-containing oligonucleotides irradiated in deuterium oxide solutions which also contain deuterated t-butanol.

Molecular models of B-form DNA containing 5-BrU, reveal that the bromine atom is in van der Waals contact with the C(2') of the deoxyribose on the 5' side of the 5-BrU moiety. This intimate contact has led to the hypothesis that hydrogen atom abstraction by the uracil-5-yl centered radical occurs from the C(2') position in DNA. These data led us to the interesting speculation regarding the source of hydrogen atoms in irradiated solutions of dinucleotides in which 5-BrU was placed on either side of a base known to transfer electrons efficiently. In this study the dinucleotides represented by 5'-BrUA-3' and 5'-ABrU-3' were synthesized. Although we had hypothesized that the yield of uracil would be greatest in 5'-ABrU-3' (since we had previously determined that electrons are capable of migrating preferentially in the 5' to 3' direction in oligonucleotides) uracil yields are not significantly different in either dinucleotide. This result is in contradiction to the hypothesis regarding abstraction of a hydrogen atom from the C(2'). However, local concentration of base moieties in dinucleotides may be significantly different in solution than base moieties tied up in oligonucleotide chains. The difference in the relative concentration profile may, in part, significantly influence hydrogen atom abstraction.

In summary, deuterium oxide and 2-methyl-2-propanol-d_{10} (deuterated t-butanol) were used to demonstrate that hydrogen atom donation can occur from different sources depending upon whether 5-BrU is irradiated as a monomer, dinucleotide, single-stranded oligonucleotide, or double-stranded oligonucleotide in solution. When irradiated as a monomer, 5-BrU captured a hydrogen atom from t-butanol. However, when 5-BrU-containing oligonucleotides were irradiated in their single- or double-stranded forms, the hydrogen atom was abstracted from the DNA molecule. These observations are consistent with the hypothesis that hydrogen atom donation occurs from the 2' carbon of the 5' neighboring deoxynucleoside to the uracil-5-yl radical located in the same strand of 5-BrU-containing DNA.

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Structural and Kinetic Studies at Model Oxide Surfaces

Bruce D. Kay and Stephen A. Joyce (Chemical Structure and Dynamics)

Project Description

The objective of this project was to examine phenomena occurring on model oxide surfaces in an effort to unravel the mechanistic details of the complex interfacial chemistry occurring in the subsurface environment. Scanning probe microscopies (scanning tunneling and atomic force microscopy) were used to study the growth and structure of model oxide surfaces. Molecular beam scattering and surface analytical techniques were used to explore the dynamics and kinetics of adsorbates interacting with these surfaces.

Technical Accomplishments

Many of the solid surfaces of interest to the environmental restoration of the soils and groundwaters at the Hanford Site are insulators in their bulk forms and thus not amenable to study with conventional electron-based surface analytical techniques. The growth of microscopically thin films on conducting substrates overcomes the electrical charging problems associated with bulk insulators. To this end we have used in situ scanning tunneling microscopy to investigate the growth and electronic properties of MgO thin films deposited on Mo(001). The films were grown by evaporating Mg metal in a background pressure of oxygen. Correct stoichiometry of the films was ensured using Auger electron spectroscopy. We have successfully studied films as thick as 25 Å, clearly demonstrating the feasibility of this method. Growth temperatures from room temperature to 750°C have been studied and drastic changes in film morphology were observed. Films grown at 300K exhibited uniform deposition with a typical grain size of ~50 Å. Film growth above 700K resulted in the formation of three-dimensional islands. These islands were aligned crystallographically with the metallic substrate. Figure 1 displays a 2000 Å x 2000 Å region of MgO film grown on Mo(001) at 700°C. The rectangular shaped islands are crystallites of MgO(100) in registry with the underlying stepped Mo substrate. The total vertical relief is ~9 Å, indicating that the films are relatively smooth over macroscopic distances.

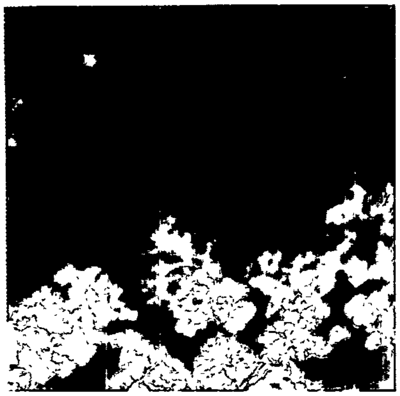

Figure 1. A 2000 Å x 2000 Å STM Image MgO Grown Epitaxially on Mo(001)

In related experiments, we studied the chemisorption of water on both thin film and bulk MgO using molecular beam scattering and surface analytical techniques. On both the thin film and bulk surfaces, water adsorbs with unit sticking probability below 140K. In both cases, the resultant thermal desorption spectra are identical, indicating that the chemical interaction of water with these two surfaces is similar. Figure 2 shows a representative temperature programmed desorption of D_2O from bulk MgO(100). The high temperature peak (240K) which saturates with increasing exposure corresponds with one water molecule adsorbed per surface Mg ion. The low temperature peak (170K) that appears with increased exposure is due to multilayer ice formation. Brucite ($Mg[OH]_2$) thermally decomposes to MgO and water at approximately 400K, suggesting that the high temperature programmed desorption feature is indicative of water molecularly bound to MgO(100). We recently developed variable energy (1 to 50 kcal/mole) supersonic molecular beams of water that will be used to resolve the molecular versus dissociative chemisorption of water on MgO.

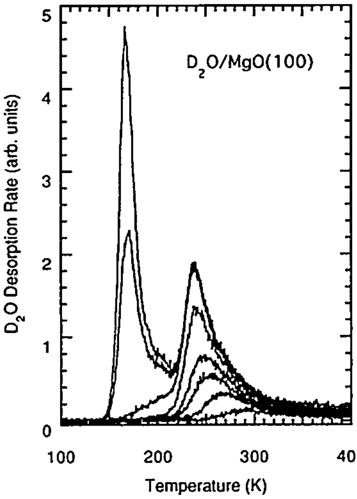

Figure 2. TPD Signal for Various Initial Coverages of D_2O on MgO(100)

Structural Studies of Modified Histone Species

David L. Springer (Biology and Chemistry)
Charles G. Edmonds (Chemical Sciences)

Project Description

In response to insult, cells are known to adjust their chromatin structure and alter their cell cycle to permit the repair and replication of damaged DNA. Our goal is to evaluate post-translational modifications to histones during the cell cycle and identify perturbations of this profile of modifications arising from chemical agents, radiation, or their combination.

Technical Accomplishments

Histones, which together with other specialized protein and DNA form the extraordinarily complex structure of chromatin, are post-translationally modified by acetylation, methylation, phosphorylation, mono- and poly(ADP) ribosylation, glycosylation, and ubiquitination. Each of these modifications is known to have important associations with alterations in chromatin structure which occur throughout the cell cycle or in response to chemical- or radiation-induced damage. The structural biology of these processes is a complex picture of protein-protein and protein-DNA associations modulated, in part, by protein post-translational modification. The full details of the changes in level of all of these modifications remains to be elucidated.

It is our premise that a fundamental understanding of the relationship of histone modification to chromatin structure and its alteration throughout cell cycle and during cell damage and repair can only be obtained by consideration of the full range of type, extent, and site of modifications. We hypothesize that the normal time-dependent profile of histone modifications through the cell cycle is nonrandom and predictable. Furthermore, this consistency will also pertain in the course of modifications arising from response to chemical or radiation insult.

We are developing methods for the evaluation of the range of histone modifications based on biochemical and mass spectrometric techniques. Initially, nuclear histones were isolated from exponentially growing cultured K562 cells, a human derived cell line. Subsequently we have begun experiments in which cell cycle synchronized populations of HeLa cells and subfractions of these populations prepared by flow cytometry are being generated for analysis. The histones are isolated from nuclei preparations, purified by reversed phase high performance liquid chromatography, and the intact protein evaluated for post-translational modification by gel electrophoresis and electrospray ionization mass spectrometry (ESI-MS). In earlier experiments on histones isolated from cultured cells exposed to sodium butyrate, we demonstrated the effect of this deacetylase inhibitor in causing significant shifts in the degree of histone acetylation. These experiments are being extended by examining histones from cells in various stages of the cell cycle obtained by synchronization. Results indicate the practicality of the determination of the time-courses of multiple histone modification, including their sequence location. Extended experiments by combined liquid chromatography-tandem ESI-MS of peptides obtained by selective proteolysis with *Staphylococcus aureus* (V8) protease or trypsin are providing specific information about the residue location of modifications. These techniques will permit, for the first time, direct analysis with high sensitivity and unambiguous evaluation of the nature and extent of multiple modification of histones as a function of cell cycle.

We have been able to demonstrate accurate mass determination of all core and linker histones present in the chromatin of chick erythrocytes. These experiments reveal the nature and extent of post-translational modification of these species. Up to this point we have relied principally on conventional linear quadrupole instrumentation. However, the use of a prototype ion cyclotron resonance instrument has demonstrated successful analysis at dramatically higher resolving power. The residue location of the observed post-translational modifications has been elucidated in tandem mass spectrometry experiments on the intact proteins, in mass spectrometric mapping experiments on the unfractionated products of selective proteolysis, and combined liquid chromatography ESI-MS of these peptides mixtures. We observe in batches of chick erythrocytes obtained from different suppliers masses for histone H2B which suggest that the protein is substantially unmodified and which differ from the predicted mass by a value of 26 daltons. This difference is not readily assigned to a simple post-translational modification and we hypothesize that these proteins may contain some unrecognized clonal difference in the respective genes. Peptide mapping experiments to test this hypothesis and to identify the nature of this variation in primary sequence are in progress. The H2A/H2B dimer and the H3/H4 tetramer isolated from the chick erythrocyte core particle have been isolated and their non-covalent structures have been examined by ESI-MS. While our experiments are still preliminary, we have not been able to demonstrate the preservation of higher order structure of these species accompanying electrospray ionization.

Our initial experiments on histones derived from chick erythrocytes have been extended to include histones isolated from human erythroleukemia-derived strain K562 grown in culture. Purification and analysis of histones derived from as few as 10^6 cells has been demonstrated. Accurate mass determination of all histones as the intact protein has permitted the recognition of amino acid sequence variants and the nature and extent of post-translational modifications. The principal modified residues observed are methylations, acetylations, and phosphorylations. In K562 cells we have found that H2B is substantially unmodified. In this case three of the known sequence variants of this protein are distinguishable in the electrospray ionization mass spectrum. Fragmentation of this intact protein in the interface of the electrospray atmosphere/vacuum interface has demonstrated prominent responses for the N-terminal 50 residues. This peptide fragment bounded at its C-terminus by a proline 51 contains two other proline residues, covering the majority of the region shown to be modified in published studies. This experiment suggests that a rapid and sensitive mass spectrometric mapping experiment for the modifications occurring in the N-terminal region of this and other histone species will be practical.

We have further extended our experiments to include cell cycle synchronized populations of HeLa cells undertaken in collaboration with Dr. N. F. Metting. Initial experiments on the histones isolated from the unsynchronized exponentially growing cultures of HeLa have afforded similar results as described above for K562 cells. Subsequently, we have examined closely synchronized populations of cells in unperturbed G1/S, G2/M, and cells arrested in G2 by γ-irradiation. We have been able to recognize differences in the nature and extent of post-translational modifications of histones in these landmark points in the cell cycle.

In earlier experiments the isolation and characterization of the histones in human diploid fibroblasts grown in culture has been undertaken in collaboration with Dr. Michael Smerdon, Department of Biophysics and Biochemistry, Washington State University, Pullman. Correlations in the nature and extent of modification of the histones occurring in this cell line as compared to those in the very rapidly proliferating K562 are consistent with the substantially lower rate of growth. On this basis this cell line appears to be a more realistic model for the patterns of post-translational modifications. However, in these experiments there appeared to be a substantially lower yield of histone species. In similar experiments on synchronized populations of fibroblast cells planned in collaboration with Dr. N. F. Metting, a significant refinement in our methodology will be required to provide the sensitivity needed for lower yield of histones. Similarly, refinement of the methods to permit the analysis of still smaller numbers of cells obtained by fractionation of cell cycle populations by flow cytometry is continuing.

We continue to interact with the larger regional, national, and international scientific community. Collaborators include: Drs. Michael Smerdon and Ralph Yount of the Department of Biophysics and Biochemistry and Dr. James Satterlee of the Department of Chemistry of Washington State University, Pullman, Washington.

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Synthesis of Site-Specific Lesions

David L. Springer, Brian D. Thrall, and Alfred F. Fuciarelli (Biology and Chemistry)

Project Description

The objective of this project was to develop molecular procedures that can be used to identify and characterize the mechanisms whereby modification of DNA by chemical carcinogens are converted into mutations and thereby initiate tumor formation. Our approach was to prepare, purify, and characterize an oligonucleotide that was site-specifically modified with 4-nitroquinoline, a highly carcinogenic compound formed as a byproduct of energy production. In addition, procedures were implemented for insertion of this oligonucleotide into larger pieces of DNA for repair, replication, and transcription studies. The repair protein UVrabc, an enzyme involved in excision repair of certain types of DNA damage including bulky chemical carcinogens like 4-nitroquinoline, was obtained from a collaborator.

Exposure of DNA to chemical agents results in structural modifications which, if left unrepaired, can lead to mutations and cancer. The mechanism whereby chemical modifications to DNA are converted to mutations and thereby initiate tumor formation is an important unanswered question in cancer research. The most successful molecular research in this area has used site- and stereo-specifically modified oligonucleotides to study DNA structure/function relationships of damaged DNA. The objective of this project was to implement methods for incorporation of lesions into DNA in a sequence-specific context and to develop capability to produce large quantities of pure, well-characterized DNA fragments. Once large quantities of highly purified modified oligonucleotide are available, spectroscopic techniques including nuclear magnetic resonance will be used to identify damage-induced structural perturbations; coupling of structural information with biochemical studies for function will contribute to our understanding of the mechanism of formation of mutations. This capability is needed to identify the impact of altered DNA structure on DNA functions including DNA repair, replication, and transcription.

Despite the importance of structure/function experiments in studies of carcinogenesis, the site-specific modification of oligonucleotides by carcinogens has been successful with a limited number of chemicals in a few laboratories. We have chosen 4-nitroquinoline-N-oxide (4-NQO) since exposure to 4-NQO forms two major DNA adducts which are predicted to lie in either the major or minor groove of DNA. Therefore, this carcinogen is an excellent model for elucidating the structural and functional consequences of damage to the major or minor groove of DNA.

Technical Accomplishments

Initially the reactive metabolic intermediate of 4-NQO, namely acetoxy-4-hydroxyamino-quinoline oxide (4-AcHAQO), was synthesized. Oligonucleotides containing a single guanine were then reacted with 4-AcHAQO (which binds primarily to guanine bases); the modified oligonucleotide was purified by high performance liquid chromatography (HPLC) techniques and characterized by spectroscopic procedures. Results from these experiments demonstrated that in addition to non-adducted oligonucleotide, two peaks were separable by HPLC methods (Figure 1). Analysis of the DNA by ultraviolet/visible spectroscopy indicated significant spectral differences between nonadducted and adducted DNA (Figure 2). The nonadducted peak had an A_{max} of 260 nm with no significant absorbance at wavelengths exceeding 320 nm. However, the adducted peak had an A_{max} of 265.5 nm and significant absorbance at 363 nm, as would be expected with modification by 4-AcHAQO. The results from these experiments demonstrate that we can produce and purify, in relatively high yield, DNA containing specific 4-AcHAQO adducts amenable to structural and molecular analysis. We have recently begun experiments to determine the efficiency at which these adducts are repaired by cellular enzymes. Additional experiments will be needed to optimize the yield of adduction, as well as to further characterize the putative adducts of interest before structural experiments are conducted.

Future studies with modified oligonucleotides will be designed to identify DNA/proteins interactions including chromatin and repair enzymes. Although ligation is a common technique used in molecular biology, our work requires high yields of large quantities of product. Thus, methods were developed for ligation of short (15 to 25 base pair) modified oligonucleotides to larger DNA fragments for structure and function studies. For this a 34-nucleotide long template was synthesized as were complementary oligonucleotides of varying lengths, one containing a single deoxyguanosine. The two complementary oligonucleotides were annealed to the template strand and ligated together under a variety of reaction conditions; at optimal conditions at least 80% of the complementary oligonucleotides were joined by covalent linkage. This technology will allow for covalent insertion of

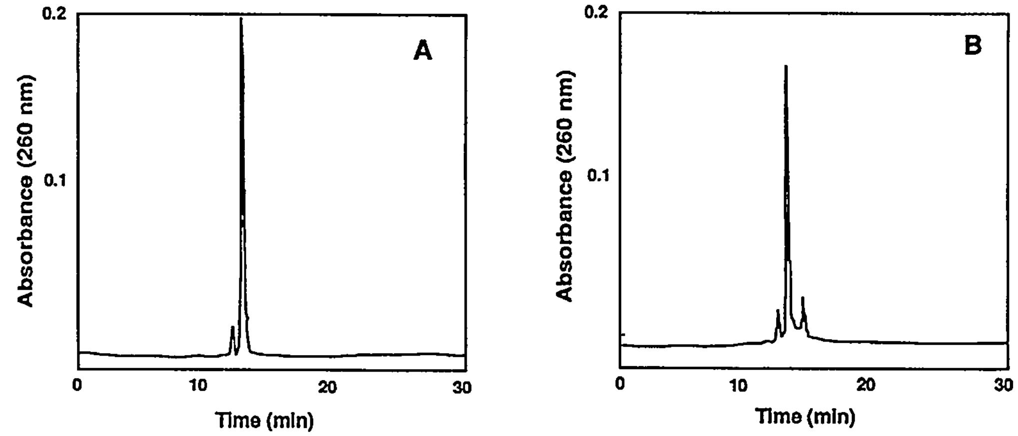

Figure 1. HPLC Chromatogram of Moc-Adducted and 4-AcHAQO Modified Oligonucleotides. An oligonucleotide (11 mer) containing a single guanine was reacted with 4-acetyl-hydroxyaminonitroquinoline-N-oxide and purified by reversed-phase HPLC in a linear gradient of methanol and phosphate buffer. Panel A is mock adducted oligonucleotide and panel B is oligonucleotide adducted with 4-AcHAQO.

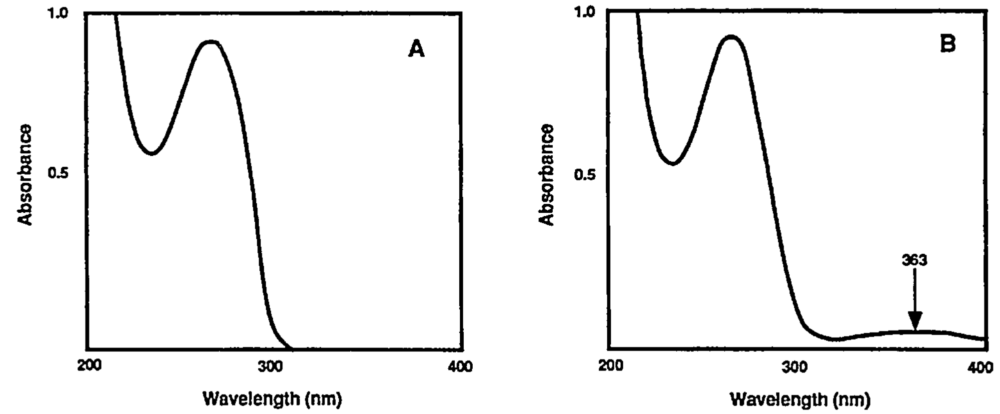

Figure 2. Ultraviolet/Visible Spectrum of HPLC Peaks 1 and 2. Oligonucleotides reacted with 4-AcHAQO were purified by HPLC and peaks 1 and 2 were collected as shown in Figure 1B. After removal of solvent, the DNA was analyzed by ultraviolet/visible spectroscopy.

site-specifically modified oligonucleotides into larger DNA fragments and plasmids for chromatin structure and repair studies.

Publication

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Technological Response

W. Brad Ashton (Global Environmental Management)

Project Description

This project investigated the fundamental forces shaping the rate and directions of long-run technological change and ways to model these factors for two important sectors—the electric power industry and agriculture. In connection with modeling-oriented tasks, the research team also investigated what is known about the general determinants of technological innovation and focused specific attention on two of these factors that are particularly important, yet poorly understood, in contemporary societies: public research and development funding and technology choice in investment decisions.

The project emphasized aspects of representing technological change in computer-based economic models, especially the prototype Pacific Northwest Laboratory Second Generation Model (SGM), which is a global general equilibrium model of the man-made sources of greenhouse gas (GHG) emissions. The purpose was to develop a Pacific Northwest Laboratory knowledge base regarding technological change that could support advanced versions of the second generation model and related policy analyses for Department of Energy program and policy organizations.

Technical Accomplishments

The technical accomplishments of this research are organized into five sections.

Factors Affecting Technological Change

An examination of the history of technological innovation indicates that a wide variety of technical, social, economic, and institutional factors have been the fundamental drivers for technological change and that these factors provide the best explanations of the significant differences in the pace and direction of such technological change that appear across different societies. The major factors behind technological innovation in one unifying study of technological innovation were described as: life expectancy, nutrition, willingness to bear risks, geographical environment, labor costs, religion, social and individual values, institutions and property rights, resistance to innovation, politics and the state, war, openness to new information, and demographic factors (Mokyr 1990). Although these factors can certainly be as important today as in the past, current technological change in wealthy industrialized nations appears to be less affected by traditional forces such as life expectancy, nutrition, and natural resource endowments. Rather, with rising standards of living and well-educated citizens, technological change is influenced heavily by economic and cultural factors such as labor costs, institutions and property rights, levels of public and private research and development funding, willingness to bear risks, and openness to new information (e.g., Mokyr 1990; Rosenberg 1976).

Technological Change in Electric Power Generation

Fossil-fuel fired steam electric generation represents a dominant portion of all the technologies employed for electricity production on both a worldwide and a national basis. Knowledge regarding technological improvements in this sector is important since fossil fuels are a leading significant source of greenhouse gas emissions.

Econometric estimates developed in this project using industry data on coal-fired steam power generation technologies over the period 1979 to 1989 (a time series analysis of cross-section data) reveal persistently positive evidence of technical progress. This finding is in sharp contrast to other historical and more varied studies from the economic production function approaches. Pacific Northwest Laboratory estimates imply that technological progress has been capital-augmenting at the rate of 1.8% per year. The composite or overall rate of technical change is found to be slightly less than 1% per annum.

A byproduct finding of the model estimation is that decreasing returns to scale exist in these technologies with respect to unit size (for instance, a 10% increase in unit scale from 750 MW to 825 MW, would cause a 12 to 13% increase in total costs).

Technological Change in Agriculture

The aim of this task was to analyze the attributes of the traditional factors of agricultural productivity and the technological change necessary to meet the food demands of the next century under the auspices of climate change. The type of agricultural model and the parameters a model would need to provide PNL's second generation model of greenhouse gas emissions with an appropriate agricultural module were also analyzed.

The research results showed that the induced innovation theory of technological change suggests that market forces play a powerful role in determining the direction of technological development, but the theory cannot explain fully the agricultural productivity growth path in developing countries. To a significant extent, government policies toward agriculture in developing countries will determine their development path. In addition to commonly known drivers of technological change in agriculture such as research and development funding, new agricultural models must incorporate strong representations of market dynamics and government agricultural policies. It was also clear that any proposed agricultural model will need to be a linked to a process-economic model because agriculture impacts the economy interactively with climate parameters. At the same time, because of regional differences in resources and stages of agricultural development, the model will need to be regionalized and provide for trade effects.

The Role of Public Research and Development in Technological Change

The objective of this task was to assess the state of knowledge regarding the impact of public sector research and development (and subsequent commercialized technologies) on private sector productivity.

This task found a great deal of work and many quantitative representations of research and development and productivity relationships, often based on production function modeling concepts. However, significant weaknesses in the knowledge base concerning how public research and development affects macro-economic performance variables like technological investment and subsequent productivity performance were apparent in this research. For instance, researchers found considerable debate about whether federally funded research and development serves to stimulate or crowd out private research and development. This means that reliable policy models of this relationship are not now possible and that more work is needed to examine the impact of federally funded research and development, by program area and by private research and development performers, on the size and direction of related private research and development. Several research concepts were suggested in the working paper documenting this work.

How Technology Choice Models Affect Technology Investment

The objective of this task is to examine the capabilities of the logit model to better represent technology choice over time and to evaluate alternative approaches. The logit framework is a type of discrete choice model that has been frequently used to model choice of technology, fuel, and transportation modes in recently developed energy and economic models. The major advantages of the logit model are that it is simple and easily implemented. However, its simplicity lies within its underlying assumptions which represent modeling limitations.

The major accomplishment of this effort was to evaluate a proposed alternative dynamic framework that improves on the logit approach in modeling technology competition over time. This new approach is better able to represent technology competition situations where the cost of competing technologies become correlated over time. It is an improvement over the logit model which has a very strict underlying assumption that the alternative remain identically and independently distributed throughout the time horizon modeled.

Conclusion

The tasks in this project found a very close association between modeling technological change and understanding productivity and economic competitiveness issues. Moreover, with PNL's increased understanding of research and development investment expenditures, considerable common ground was found to exist between technical progress and economic growth. Pacific Northwest Laboratory researchers have now demonstrated an in-depth understanding of technological innovation and improved technical capabilities to make substantive contributions to many technology policy issues surrounding global climate change and alternative energy/economic growth paths.

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D. Kavanaugh. 1994. "Technical Progress in Renewable Electric Energy Technologies." PNL working paper to be submitted to *Energy and Environment*. Multi-Science, United Kingdom.

Presentation

D. Kavanaugh. 1993. "Technical Progress in Renewable Electric Energy Technologies." Presented at the 15th North American Conference of the International Association of Energy Economics, Seattle, Washington, October.

Other Accomplishments

Craig Diamond, Pam Brockmeyer, and Jennifer Friedman (PNL staff member on educational leave during FY 1994) are students that were supported by this research.

The Effect of Individual Alpha Particle Tracks on Expression of Regulatory Proteins in Individual Cells

Noelle F. Metting (Biology and Chemistry)

Project Description

The objective of this project was to measure the intracellular localization of several cell-cycle regulatory proteins in individual mammalian cells, and begin to measure changes in localization after the passage of a single alpha particle through the cell.

The transition from the premitotic G2-phase into mitosis in dividing mammalian cells is dependent on the kinase activity of the cdc2-cyclin B protein complex. For cultures irradiated by moderate doses of x-rays or alpha particles, there is a transient failure of the complex to activate, by way of dephosphorylation of the cdc2 subunit, which correlates with the duration of radiation-induced G2-arrest. The data support the hypothesis that radiation-induced delay in cdc2 activation is caused by, or effects, alteration of the normal cellular compartmentalization of the proteins. To test this hypothesis, we have developed the capability to measure the intracellular localization of several cell-cycle regulatory proteins in individual mammalian cells, and have begun to measure changes in localization after x-irradiation.

Ionizing radiation causes a division delay in most mammalian cell types, which is dominated by a period of G2 arrest. The magnitude of the delay is dependent upon the type of cell, the position of the cell in the replication cycle, the dose, and the linear energy transfer of the radiation. The length of G2 arrest increases linearly with dose, and the relative biological effectiveness of the length of G2 arrest is LET-dependent with a maximum (RBE_{50} about 8.0) at about 100 keV/um. In all eukaryotic cells studied, it has been shown that cdc2 is a central cell cycle regulator protein. It is the catalytic subunit of a serine/threonine protein kinase, a complex which also includes one of several cyclins, and whose kinase activity has been shown to vary as a function of cell cycle position, rising from low levels in G1-S to peak in G2-M. This kinase activity is correlated with the phosphorylation state of cdc2, and is dependent on the presence of the cyclin. The fission yeast protein tyrosine kinase, wee1, has been shown to be necessary for inactivation of cdc2, and it is also required for radiation-induced mitotic delay. The abrupt activation of the cdc2 kinase at the beginning of mitosis is correlated with dephosphorylation of two cdc2 amino acid residues, generally thought to be mediated by the tyrosine phosphatase cdc25. Mammalian proteins have been found that are homologous to wee1 and cdc25, as well as other proteins implicated in the network of cell-cycle control.

Several recent papers have discussed radiation-induced G2-arrest in terms of these cell-cycle regulating proteins. Pre-synchronized HeLa cell cultures that were given high doses of radiation (6 to 10 Gy) show G2-arrest owing to insufficient cyclin B protein. This was caused by inhibition of gene transcription when the cells were irradiated in S-phase, or by inhibition of both gene transcription and mRNA translation when irradiated in G2. I have recently shown that radiation-induced G2 arrest after moderate doses of x-rays (2.0 Gy) or alpha particles (0.2 Gy) is caused by the transient failure of the cdc2-cyclin B1 complex to dephosphorylate and thus become active (doctoral thesis work, manuscript in preparation). Both cyclin B1 and cdc2 proteins are present in abundance, as are the wee1 kinase and cdc25 phosphatase which specifically regulate the phosphorylation state of cdc2.

A possible mechanism for radiation-induced delay in cdc2 activation is the up-regulation of the inactivating wee1 kinase, either directly or by way of its own modulating network of phosphatase(s) and kinase(s). Unscheduled phosphorylation (or dephosphorylation) of a component of the cell-cycle regulatory network could cause a perturbation in the cellular compartmentalization of certain proteins. Cyclin B accumulates in the cytoplasm of interphase cells (shown in both HeLa cells and human foreskin fibroblasts) and is associated with cdc2 in the cytoplasm, only entering the nucleus at the beginning of mitosis before nuclear lamina breakdown. In human cells, cdc25c was found to be primarily localized in the nucleus, suggesting that the initial activation of the cdc2-cyclin B complex is a nuclear event. It is not known for certain if activation of the complex occurs in the cytoplasm or the nucleus. My hypothesis is that the radiation-induced delay in cdc2 activation may cause, or is an effect of, alteration of the normal cellular compartmentalization of the proteins.

Technical Accomplishments

In the first year of this project, time was spent refining specific processes involved in working with the single particle/single cell irradiator in order to make the irradiation procedure compatible with the requirements of in situ protein localization assays. These processes include assembly of special mylar bottom dishes, plating of cells, cell-by-cell irradiation, subsequent handling of cells. Other necessary techniques were learned, such as immunocytochemistry, fluorescence microscopy, and flow cytometry. Experiments were conducted to determine optimal values of parameters, such as fixation and permeabilization times, and primary antibody buffer concentrations for the various antibodies used in immunostaining.

Preliminary experiments using synchronized HeLa cells and x-irradiation have been started and are presently ongoing. In addition, cells have been irradiated through the nucleus using the single particle irradiator. We demonstrated that both control and irradiated cells showed a different morphology, a much more rounded shape on the mylar dishes than that seen on either glass slides or polystyrene culture dishes. Because the assay is dependent on showing protein localization in relation to the cell nuclear membrane, we plan on using confocal microscopic techniques in the future.

Presentation

N. F. Metting. 1994. "Specific Transcript Induction and Protein Localization of Cell-Cycle Regulators after α-Particle Irradiation." Presented at the Charged Particle Microbeam Applications Workshop, Richland, Washington, October 10-12 (invited paper).

Tumor Formation in Cells and Tissues Studied by Means of Liquid-State and Solid-State NMR

Robert A. Wind (Macromolecular Structure and Dynamics)

Project Description

The main objective of the research is to improve the capabilities of nuclear magnetic resonance (NMR) in cancer research. To this end, existing liquid-state nuclear magnetic resonance methodologies will be executed in larger external fields than are used today, high-resolution solid-state nuclear magnetic resonance will be performed on frozen samples, and multi-nuclear nuclear magnetic resonance will be applied. The nuclear magnetic resonance research will be used for the detection and characterization of preneoplastic and neoplastic lesions in inbred rodents exposed to toxic chemicals and/or ionizing radiation. It will be investigated whether this research can result in a detection of these lesions in earlier stages of the carcinogenic process and for lower dose levels of exposure than is possible today. If successful, the proposed technology has the potential of making important contributions to both medical and health-related environmental research.

The potential importance of nuclear magnetic resonance for the detection and characterization of tumors has long been recognized. It has been found that several parameters that can be determined by nuclear magnetic resonance are different in healthy and tumorous tissues. Examples are the water proton T_1 and T_2 values and the intensities of the water-soluble metabolites. However, the results are ambiguous, as many different types of tumors and other lesions give similar results, and as a large scatter in the results often makes the differentiation between healthy and tumorous tissues difficult. We will undertake several approaches which might improve this situation significantly: 1) we will extend the existing nuclear magnetic resonance methodologies to higher fields; 2) we will perform high-resolution solid-state experiments on frozen samples. This makes it possible to investigate structures and dynamics of large-molecular weight molecules such as phospholipids, proteins, and nucleic acids, which form a significant fraction of the total amount of biological material, but which cannot be observed with liquid-state nuclear magnetic resonance techniques; 3) it will be investigated under which experimental conditions the differentiation between healthy and tumorous cells and tissues becomes maximal, and whether a combination of liquid-state and solid-state nuclear magnetic resonance parameters will lead to improved tumor detection and characterization; 4) we will perform our experiments on cells and tissues obtained from model inbred rodent lines.

Technical Accomplishments

In FY 1994 we started a liquid-state ^1H and ^{13}C nuclear magnetic resonance study and a solid-state high-resolution ^{13}C study of healthy mammary tissues obtained from female Fischer rats, and of R3230AC mammary tumors implanted in the animals and removed three weeks after implantation (one of the reasons of choosing these samples is the short time it takes to get tumors which made it possible to get first results quickly). The liquid-state nuclear magnetic resonance experiments were performed at 4°C in magnetic fields of 11.7 tesla (500 MHz proton frequency and 125 MHz carbon frequency) and 17.6 tesla (750 MHz proton frequency and 187 MHz carbon frequency). The solid-state experiments were carried out at -100°C in a field of 7 tesla, corresponding to a proton frequency of 300 MHz and a carbon frequency of 75 MHz. Following are the first results.

Liquid-state nuclear magnetic resonance experiments:

- The spectral resolution of the ^{13}C spectra is the same at both magnetic fields, whereas the spectral resolution of the ^1H spectra marginally increased at 17.6 tesla.
- A very large water peak is observed in the ^1H spectra of the tumors because the tumors consists mainly of cancer cells, which have a water content of more than 90%. The water peak is relatively small in the healthy tissues, which are mainly adipose tissues.
- The T_1 value of the water line in the proton spectra is about 1.4 second, both for the healthy and tumorous tissues, and independent of the field. This differs from the literature results, where T_1 is found to increase in tumors. The reason probably is that usually in the literature the T_1 of the total proton intensity is measured rather than that of the water line only, and that in the healthy tissue this total intensity is mainly due to the faster relaxing protons present in the adipose tissue.
- The T_2 value of the water line in the proton spectra is larger in the tumorous tissue, in accordance with the findings in the literature.

- A two-dimensional heteronuclear ^{1}H - ^{13}C cross-correlation experiment has been carried out, which made it possible to relate the various proton lines with the corresponding carbon lines, and to assign the proton lines using the assignments of the carbon lines given in the literature.

- Figure 1 shows ^{13}C spectra obtained in healthy and tumorous tissues. In these spectra mainly the adipose tissues are observed. This makes the experiments on the tumorous tissues, which contain only a small percentage of adipose tissue, very time consuming. The intensity ratios of some peaks in the spectra are different for the two types of tissue, and extra peaks are observed in the tumor. This is in general accordance with findings in the literature (T. A. Victor et al. 1993. *Br. J. Cancer*, 68, 336).

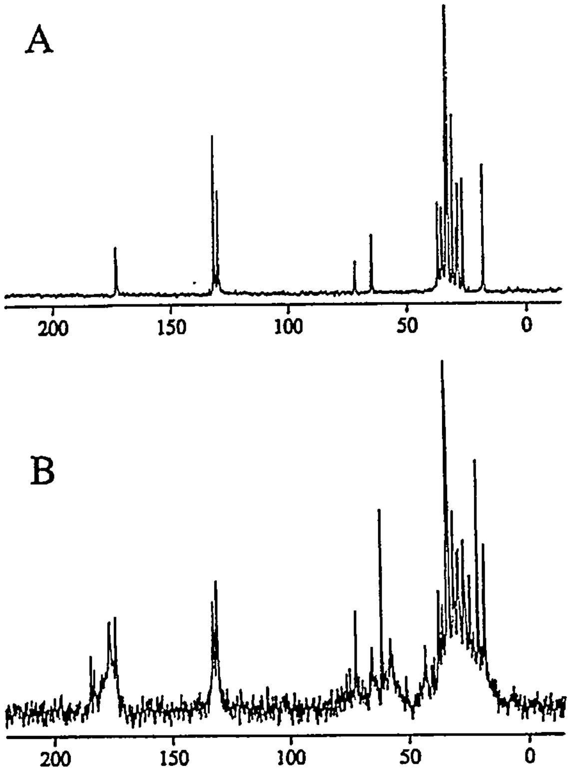


Figure 1. ^{13}C Bloch Decay Spectra Obtained at 4°C. A: healthy mammary tissue; B: mammary tumor tissue.

High-resolution solid-state nuclear magnetic resonance experiments:

Figure 2 shows the ^{13}C spectra of a healthy and tumorous tissue, obtained at -100°C, using a special technique called cross-polarization magic-angle spinning (CPMAS). This technique makes it possible to obtain nuclear magnetic resonance spectra with a (for solids) large spectral resolution. It follows that the spectrum of the healthy tissue is very similar to that observed via liquid-state nuclear magnetic resonance (the main difference is that less spectral resolution is observed, which is inherent to measuring in the solid state). However, the solids spectrum of the tumor is completely different from that observed in the liquid state. The reason is that, as mentioned, the tumor consists of more than 95% of cells, and a large fraction of the cells consists of large, relatively immobile, molecules, which cannot be measured by liquid-state nuclear magnetic resonance. With solid-state nuclear magnetic resonance techniques such as CPMAS these compounds become observable and, in fact, dominate the ^{13}C lines originating from the small residual adipose fraction (this also explains the finding that the solid-state spectra of the tumors could be obtained in a much shorter time than the liquids spectra).

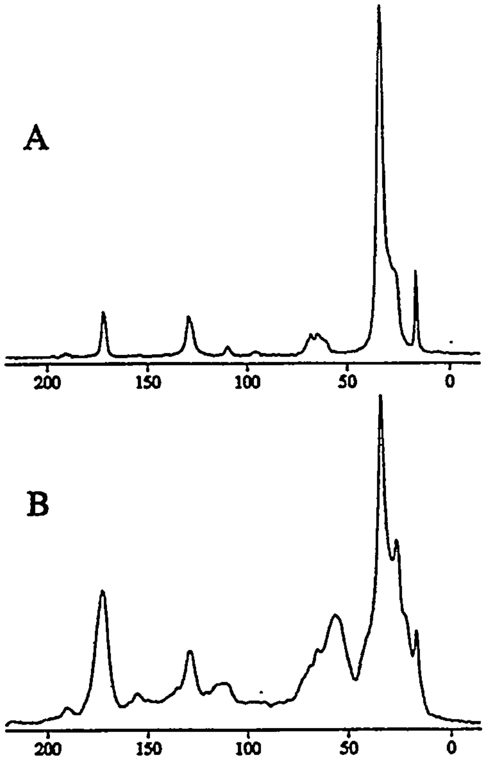


Figure 2. ^{13}C CPMAS Spectra Obtained at -100°C. A: healthy mammary tissue; B: mammary tumor tissue.

Compared to liquid-state nuclear magnetic resonance, solid-state nuclear magnetic resonance has some important advantages:

- With solid-state nuclear magnetic resonance much larger differences are observed between healthy and tumorous tissues than with liquid-state nuclear magnetic resonance. This might result in an improved diagnosis of cancer.

- Solid-state nuclear magnetic resonance makes it possible to observe the large-molecular weight components of cells. As the carcinogenic process occurs because of a transformation of (the initially small fraction of) epithelial cells into malignant cells, this makes solid-state nuclear magnetic resonance the method of choice to study the changes in the structures and dynamics of cells during their transformation. This might contribute to an improved understanding of the carcinogenic mechanisms on a cellular level.

Presentation

R. A. Santos, B. A. Concannon, D. R. Fisher, K. M. Groch, and R. A. Wind. 1994. "NMR, MRI, and Tumor Formation." Presented at the Rocky Mountain Conference, Denver, Colorado.

Uncertainty Analysis for Computer Models

Albert M. Liebetrau (Analytic Sciences and Engineering)

Project Description

The purpose of this project was to continue development of practical methods of sensitivity and uncertainty analysis for complex computer codes that have either a large number of input variables or extremely long run times. The methods are especially intended for system codes that involve the linking of several codes with these properties. The proposed work had two aspects, 1) to develop efficient sampling designs for simulation, and 2) to develop computationally tractable approximations to the (output) response surfaces of the models in question. Efficient input designs reduce computing times by minimizing the number of statistical modeling and display runs required. The approximations were used to perform simulations that would otherwise be prohibitive because of the long run times involved. Essential properties of the approximation are that it preserve the essential features of the underlying code, and that it run much faster than its complex counterpart.

Human and earth systems are extremely complex processes. The modeling of these systems to assess the effects of climate change is an activity fraught with uncertainty. System models typically involve linking a series of computer codes, each of which is a detailed model of some physical or social process. In such system models, the output from one process model is the input to another. Traditional methods of uncertainty analysis are inadequate because of the sheer complexity of the modeling effort: Monte Carlo methods and the exhaustive evaluation of "what if?" scenarios to estimate sensitivities fail because of the heavy computational burden. This research was undertaken to develop more efficient methods for learning about and performing uncertainty analyses with system models that are constructed from a collection of computer codes.

Technical Accomplishments

Under this project, we began development on a two-tiered strategy for uncertainty analysis for systems of computer-intensive codes. The basic idea is to develop computationally less demanding approximations to the underlying codes that could be used for most uncertainty calculations. The three major elements of this strategy were selection of an initial set of inputs to run the underlying code (the design step), development of a suitable approximation to the response surface of the underlying code (the approximation step), and the use of information from existing runs to determine the optimal locations for additional runs of the underlying code (the updating step).

Our research has shown that acceptable procedures exist for designing the set of initial runs of the underlying codes. Latin hypercube sampling (LHS) is one widely used design strategy that has proved very effective for sensitivity and uncertainty analysis. Consequently, we have used Latin hypercube sampling to select initial runs and have concentrated our efforts on the approximation step.

A first step was to identify potentially useful strategies for approximating the response surface of the underlying code. We have continued to work with two approximations methods that were selected last year: the MARS procedure, which involves the use of multivariate adaptive regression splines; and the TREES procedure, which involves the regression trees. Both procedures can be described as constrained linear optimization procedures.

Both approximation methods were applied to two codes, the erosion productivity import calculator (EPIC) code and the Advanced Repository Source Term (AREST) code. Each code has characteristics typical of codes used to simulate some system or process: the EPIC code was used in the MINK (Missouri, Iowa, Nebraska, and Kansas) study to simulate crop production for a variety of climate scenarios; and the AREST code was developed to simulate the containment and release performance of a geologic repository for radioactive wastes. The response of the EPIC code is quite linear over regions of interest, but the output is truly stochastic. On the other hand, the AREST code is highly nonlinear but it can be run in a deterministic mode. The AREST code estimates releases of radionuclides, which, of course, must be non-negative.

The MARS approximation procedure is attractive because it yields an approximation of minimal complexity (under specified constraints) for a given set of runs of the underlying code. A second desirable feature is that variance estimates computed from the MARS approximating surface were not significantly different than those computed directly from the underlying model. We discovered, however, that the MARS procedure did not work well when the response surface of the underlying model was constrained. Regression trees worked better for dealing with the "hard" zeros which are a unique feature of the AREST code (but typical of many physical or chemical processes). The results of this work suggest that a variety of approximation methods will be required to obtain suitable approximations to the many different codes that will likely be encountered in practice.

The expertise gained from the initial exercises described above has been (and is being) tested and expanded in several application. MARS approximations to the EPIC code have been used to develop a model (MINK 0.0, publication) to assess the regional-scale economic effect of climate change. The model does remarkably well at reproducing the results of the MINK study. We have begun developing the approximations required to extend this methodology to the entire United States for use in connection with the GCAM model. For this application, we investigated the effects of various input correlation structures on the resulting EPIC code approximations. The methods developed under this project will also be used in the uncertainty analysis component of a performance assessment of the proposed high-level radioactive waste repository at Yucca Mountain, Nevada.

We have also started to investigate wavelets as a third method for developing response surface approximations. The attractive feature of a wavelet approximation is that it consists of sums of functions that are built up in a hierarchical fashion. This feature allows the investigator to work at various scales of approximation. Moreover, the wavelet approximator is useful for updating because when additional runs of the underlying code become available, it can be updated "locally," (i.e., by recalculating the approximation in the neighborhood of the new point). By way of contrast, the MARS and TREES approximators must be recomputed for the entire surface when new points become available. Determining the feasibility of wavelet methods for model approximation will be a primary focus of future work.

Publication

M. J. Scott, A. M. Liebetrau, and C. A. LoPresti. 1993. "Climate Uncertainty and the Regional Economic Impacts of Global Climate Change." In *Proceedings of the Thirty-Second Hanford Symposium on Health and the Environment*, Richland, Washington, 19-21 October.

Presentation

A. M. Liebetrau and M. P. Pokorny. 1994. "Computational Analogues to Complex Computer-Based Codes." Presented at the Fifth International Conference on Statistical Methods for the Environmental Sciences in Burlington, Ontario Canada, 11-15 August, to be submitted to *Environmetrics*.

Use of Proliferating Cell Nuclear Antigen (PCNA) to Quantify Cell Proliferation in Respiratory Tract and Other Target Tissues of Rodents Inhaling Xenobiotics

Roger A. Renne (Toxicology)

Project Description

The objective of this project was to improve our capability to identify and quantify cells proliferating in target tissues of laboratory animals as a result of exposure to radiation or toxic chemicals, and to use this information to study the relationships between cell proliferation and cancer induced by physical or chemical insults.

Technical Accomplishments

We further refined the assay using a monoclonal antibody against proliferating cell nuclear antigen (PCNA) to measure cell proliferation in the respiratory tract of rodents inhaling xenobiotics. In FY 1994, we compared the use of two commercially available monoclonal antibodies (PC 10 and 19A2) against PCNA for measuring cell proliferation in the upper respiratory tract of rats exposed to a test chemical for 18 months. This was an extension of the work performed on these same tissues in FY 1993. We prepared replicate slides from the same tissues used in our 1993 work, and ran duplicate PCNA assays on these tissues using the PC 10 antibody (same antibody as used in 1993), and the 19A2 antibody, another commercially available anti-rat PCNA antibody used for studies in rodents. We counted labeled surface epithelial nuclei from four areas of the nasal cavity of rats exposed to one of three concentrations of a test chemical, and from unexposed control rats.

Figures 1 through 4 illustrate the results of counting labeled nuclei in these four areas from exposed and control rats. Figure 1 represents the surface respiratory epithelium lining the nasal turbinates on both sides of the nose in sections of nasal cavity taken at a point just caudal to the upper incisor teeth. Figure 2 is the surface epithelium on both sides of the median septum at the same level. Figure 3 represents the olfactory epithelium lining the dorsal meatus bilaterally at the level of the incisive papilla. Figure 4 represents the olfactory epithelium lining the dorsal meatus at the level of the first upper molar teeth.

The data illustrated in Figures 1 and 2 indicate that both antibodies readily label nuclei from proliferating surface respiratory nasal epithelium, but PC 10 antibody increases labeling rate considerably, compared with 19A2. The data on olfactory epithelium (Figures 3 and 4) indicate no clear differences except in rats exposed to the highest concentration of the test chemical, in which labeling with PC 10 was much greater at level 2.

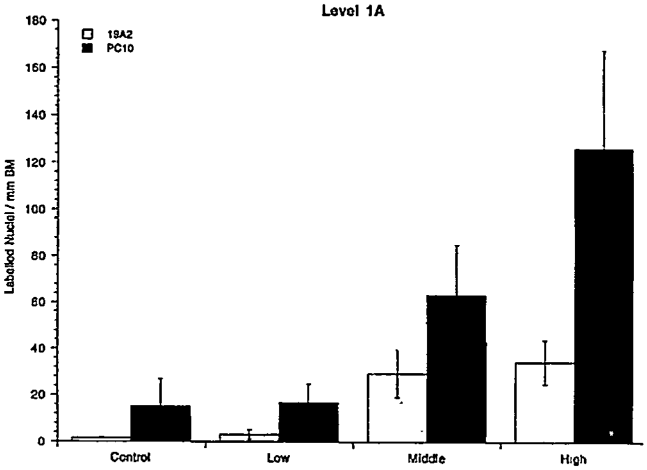


Figure 1. Labeling rates for anti-PCNA antibodies in respiratory epithelium lining the nasal turbinates of rats chronically exposed to a nasal irritant.

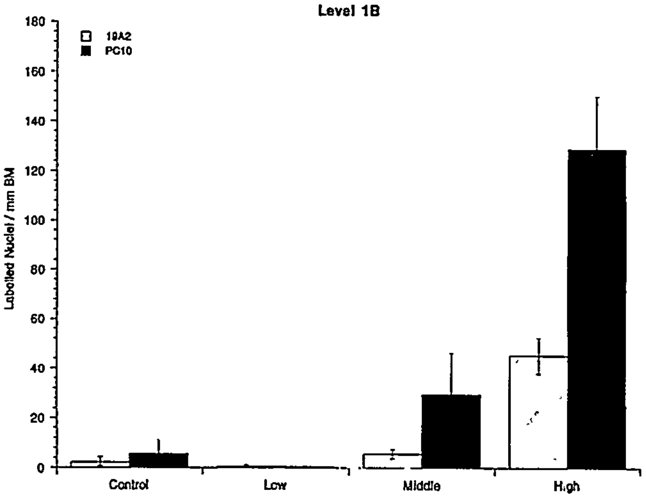


Figure 2. Labeling rates for anti-PCNA antibodies in respiratory epithelium lining the median nasal septum of rats chronically exposed to a nasal irritant.

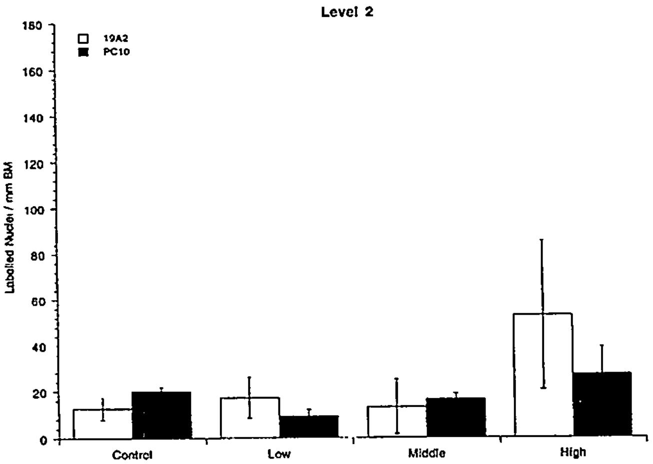


Figure 3. Labeling rates for anti-PCNA antibodies in olfactory epithelium lining the rostral nose of rats chronically exposed to a nasal irritant.

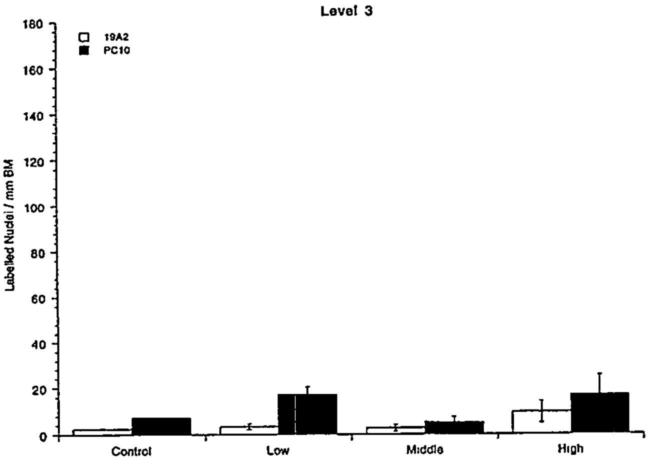


Figure 4. Labeling rates for anti-PCNA antibodies in olfactory epithelium lining the caudal nose of rats chronically exposed to a nasal irritant.

Presentation

We presented a poster describing our PCNA studies on rat at Research Triangle Park, North Carolina, September 20-23, 1993. The proceedings of this conference, including an extended abstract of our poster presentation, are in press in *Inhalation Toxicology*.

Valuation of Non-Glamorous Natural Resources

Gordon R. Bilyard (Technology Analysis Planning Center)

Project Description

At present, it is not possible to effectively compare the socioeconomic values of natural resources based on widely recognized services to man with the intrinsic values of natural resources based primarily either on services to natural systems or on poorly recognized services to humans. Although methods presently exist for determining harvest values, recreational values, and some intrinsic values (such as scenic quality) that natural resources provide, no comparable methods presently exist for valuing functions or services of natural resources in ecological systems. The most important of this latter set of functions and services are ecological function (e.g., productivity and nutrient cycling). In addition, non-glamorous resources may provide services to humans that are mundane, overlooked, undervalued, or not valued at all (e.g., pollution-holding capacities of riparian zones that reduce the need for water treatment downstream, or soil stabilization properties of vegetative cover that reduce the need for habitat restoration). As a result of the inability to compare these two subsets of functions and services effectively, it is difficult to make confident and defensible decisions regarding tradeoffs among alternative actions that involve or impact the environment.

This research attempted to provide an inexpensive, easily communicated, prescriptive process whereby scientists and economists could evaluate non-glamorous resources in economic terms that are directly comparable with more traditional economic analyses that address human economic systems. Non-glamorous natural resources are herein defined as those resources that are functionally important to ecosystems, but are not usually perceived as providing direct service to humans. This definition excludes endangered species, species of known commercial and recreational value such as salmon, and "unique" areas valued as heritage areas—like Glacier National Park.

A conceptual model of a valuation process that defines the upper and lower limits of the service values of natural resources, and that "interpolates" between those limits for the purpose of deriving realistic service values was developed and tested during this research. The shrub steppe habitat of eastern Washington was chosen as a test case for this valuation process, for several reasons: it qualifies as "non-glamorous," it (or a similar habitat type) is found on DOE sites throughout the west, and sufficient scientific and economic data were available to test the conceptual model.

Technical Accomplishments

When the conceptual model was applied to shrub steppe habitat, it was found that human analogs for functional attributes of ecosystems exist in some cases, but not others. For those cases where no human analogs exist, it was not possible to "interpolate" between the upper and lower limits of service values. However, for functions where human analogs do exist, it was often possible to provide this interpolation function through creative use of existing economic valuation methodologies. It was also possible to further define the strengths and weaknesses of various "willingness to pay" methodologies, including the Contingent Valuation Methodology that is being proposed for determining Natural Resource Damage Assessment claims under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

General findings were that "developed" uses of land and the associated habitat disturbances (e.g., farming, grazing, residential housing) have values that are mutually exclusive. However, "undeveloped" uses of land that wholly or mostly preserve land, its associated habitat, and its inherent functions and services (e.g., recreation, soil stability, biological diversity, education) have values that are additive. In the "undeveloped" state, the cumulative values of these functions may exceed the values of the mutually exclusive "developed" uses. Moreover, different "developed" uses negatively affect ecosystem function, and hence the cumulative values of the ecosystem in different ways. Given a good understanding of the cumulative value of the "undeveloped" land, the conceptual model allows one to determine when the value of the land and associated habitat in the "undeveloped" state exceeds the value of the land for a given "developed" alternative use.

Specific to shrub steppe habitat, it was found that the soil stabilization function and the biodiversity function associated with the "undeveloped" state could each on their own outweigh dryland farming at the margin, were markets available with which to express the preferences of people bearing the costs of traffic hazards or extra household cleaning, or who value species diversity functions.

Because the bulk of the shrub steppe value was found to be in the soil stabilization function, it was found that only farmed land, overgrazed land, and urban building sites (temporarily) could cause the offsite damage that would account for the bulk of that habitat's value. Although those and other "developed" uses could be managed to maintain soil stability, the biodiversity function and associated value could still be lost. Critically for shrub steppe habitat, the value of the biodiversity function cannot be mitigated for technical reasons.

Publication

M. J. Scott et al. "Valuation of Non-Glamorous Natural Resources." (To be submitted to a peer-reviewed journal.)

X-Ray Absorption Fine Structure

Steve M. Heald (Environmental Science Research Center)

Project Description

This project supports the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) in the creation of an advanced x-ray microprobe, and other advanced x-ray absorption fine structure (XAFS) capabilities. The intent of this research is to develop new techniques that push x-ray methods to new realms of spatial resolution. The effort involves both support of the PNC-CAT in the development of these capabilities at the Advanced Photon Source, and establish proof-of-principle for these methods on problems of importance to environmental research.

Technical Accomplishments

The new generation of synchrotron radiation sources such as the Advanced Photon Source (APS) at Argonne National Laboratory offers x-ray beams of unprecedented brilliance. These beams are well suited to applications such as an x-ray microprobe. If suitable optics are developed, submicron x-ray beams can be developed with intensities similar to the millimeter sized beams at current x-ray sources. Such microbeams allow advanced x-ray methods to be applied to complex and fine-grained materials, and provide imaging capabilities complementary to standard optical electron based methods. To develop this unique resource, a group of Pacific Northwest and Canadian institutions formed the PNC-CAT. In past years, this group has been successful in being chosen by the Advanced Photon Source to develop a sector, and developed a conceptual design which was approved. During FY 1994, this design was refined and a detailed engineering effort was begun. The design effort includes PNL staff and engineers from the University of Washington supported by subcontract to this program. A second aspect of the program is the application of advanced x-ray methods to problems of importance to environmental research using existing synchrotron sources. This allows us to be fully prepared to use the Advanced Photon Source facilities when they become available.

Progress in the beam-line development has been substantial. Many options for the basic beam-line design have been studied using ray-tracing, and the design is now reaching its final configuration. Similarly, extensive modeling has been carried out for various microfocusing options, concentrating on the use of tapered capillary optics. These studies show that we can achieve intensities of 10^{10}-10^{11} photons/sec/μm^2. This means that the full range of experiments currently being carried out on millimeter sized samples will be possible on the microscopic scale. In view of these results, we have hired a postdoctoral fellow to begin fabricating tapered capillaries using facilities available at the PNL glass shop. While other groups are also fabricating capillaries, our effort is unique in that we have access to advanced fiber optic facilities which should allow the production of the long capillaries needed for optimum use of the Advanced Photon Source.

In preparation for the eventual completion of the Advanced Photon Source beam line, experimental work is being carried out at the National Synchrotron Light Source (NSLS) and elsewhere. Members of this program have been actively involved with several PNL groups. We have been involved with the first structural measurements of ion hydration in supercritical water solutions using XAFS. The results reveal a clear change in ion coordination as the water pressure is changed. Supercritical water is a promising solvent for a variety of hazardous waste destruction processes. Another research area is in the geochemistry of micas. Measurements of the structural changes accompanying oxidation of iron in biotite mica are expected to provide understanding of the natural processes which transform micas into clay type minerals. Preliminary work on ion complexing in dilute leachate solutions was also started. These are challenging experiments for current generation beam lines, but early results indicate that with improved beam lines and detectors they should be relatively straightforward. Exploratory work has also begun at the Synchrotron Radiation Source (SRS) in Madison, Wisconsin. This is a convenient facility for measurements of chemistry and bonding of silicon and aluminum, two very important elements in many minerals. Initial measurements on silicon were very promising, and work on aluminum is planned soon.

This program has also supported pioneering studies into the use of x-ray resonance inelastic scattering (XRIS) as an electronic and structural probe. This technique exploits the interference between the x-ray absorption and emission processes to 1) extract structural information analogous to XAFS, but with advantages for large bond lengths and 2) determine the electronic momentum resolved x-ray absorption and emission spectra for band structure determination, and studies of collective phenomena. To fully exploit this technique, a high resolution angle resolved x-ray spectrometer is needed.

Publications

P. D. Johnson and Y. Ma. 1994. "Band Structure and x-ray Resonant Inelastic Scattering." *Phys. Rev.* B49, 5024.

Y. Ma. 1994. "X-ray Absorption, Emission, and Resonant Inelastic Scattering." *Phys. Rev.* B49, 5799.

Y. Ma. "Structure Determination Using X-ray Fluorescence Interferometry." *Chem. Phys. Lett.* (in press).

Y. Ma and M. Blume. "Interference of Fluorescence X-rays and Coherent Excitation of Core Levels." *Rev. Sci. Instrum.* (in press).

Y. Ma, P. Skytt, N. Wassdahl, P. Glans, J. Guo, and J. Nordgren. 1993. "Core Excitons and Vibronic Coupling in Diamond and Graphite." *Phys. Rev. Lett.* 71, 3725.

K. F. Voss, K. H. Kim, E. A. Stern, F. C. Brown, and S. M. Heald. 1994. "A Capillary Concentrator for an X-ray Microprobe." *Nucl. Instrum. and Methods* 347A, 390.

Presentations

S. M. Heald, J. E. Amonette, G. D. Turner, and A. D. Scott. 1994. "An XAFS Study of the Oxidation of Structural Iron in Biotite Mica by Solutions Containing Br_2 or H_2O_2." Presented at the 7th International Conference on XAFS, Berlin, Germany.

Y. Ma. 1994. "Core Exciton and Vibronic Coupling in Diamond and Graphite." Presented at the American Physics Society, March Meeting, Pittsburgh.

Y. Ma. 1994. "X-ray Resonant Inelastic Scattering." Presented at the 7th International Conference on XAFS, Berlin, Germany.

2.0 Process Science and Engineering

Advanced Catalysts and Catalytic Processes

Thomas D. Brewer (Materials Sciences)

Project Description

The objective of this project was to develop solid acid catalysts that eventually can be used on an industrial scale to upgrade fossil fuels. Jointly conducted by PNL staff in collaboration with Washington State University, the project involves materials synthesis, characterization, and catalytic properties assessment. New synthetic methods are being devised, and existing methods are being altered, to tailor the surfaces of appropriate metal oxides to yield highly acidic surface sites. The synthesized and modified materials are characterized to more fully understand the nature of the catalytically active acid sites, then screened with respect to their activity and selectivity in catalyzing isomerization and alkylation reactions.

Technical Accomplishments

Prior scientific/technical efforts were directed toward synthesizing acid-treated aluminosilicates, titanates, and other metal oxides which were prepared by the glycine-nitrate process. These materials showed low catalytic activity for the isomerization of n-butane to isobutane due to the inability of the acid anions to react with the substrate surface. However, sulfated metal oxide catalysts containing titanium, zirconium, hafnium, iron, and tin have been synthesized through hydrolysis of the respective metal salts at elevated pH. We have determined the optimum hydrolysis pH to be between 8 and 9 and the optimum sulfuric acid concentration to deposit the sulfate anion on the surface to be between 0.5 and 1.0 molar.

As a result of thermal and dynamic x-ray diffraction studies performed at Washington State University and Hammett indicator tests, the precipitated metal hydroxides appear to need a thermal treatment to remove water molecules adsorbed onto the surface. However, the thermal treatment should not be of sufficient temperature or time to remove hydroxyl groups and their related Bronsted acidity. If the hydroxyl groups are removed or condensed prior to sulfation, the metal oxide crystallizes and forms a stable phase which is resistant to sulfation. The resulting dehydroxylated materials, after sulfation, have proven to be ineffective n-butane isomerization catalysts. If the metal hydroxide is thermally treated at a temperature and time sufficient to remove water but not hydroxyl groups, the resulting material can be sulfated with 0.5 to 1.0 molar sulfuric acid, followed by a final heat treatment which condenses the sulfate group onto the crystallized metal oxide lattice.

Infrared analysis studies have shown that the sulfate anion initially coordinates to the metal oxide surface in a bidentate, or metal oxide bridging, mode. As the final heat treatment temperature increases, the bridging bidentate peak gradually shifts to a chelating peak. Thermal gravimetric analyses have indicated an initial weight loss of the sulfated metal oxide materials due to the desorption of physically adsorbed water, followed by a second weight loss most likely due to decomposition of the acid and liberation of sulfur trioxide.

Sulfated zirconia catalytic materials have shown n-butane isomerization conversions between 57 and 45% over a 15 minute run at 200°C and a 0.2 minute residence time. For comparison, a commercially supplied sulfated zirconia catalyst showed between 60 and 34% conversion using the same reaction conditions.

Sulfated zirconia's catalytic activity results show it to be the superior n-butane isomerization catalyst of the five sulfated metal oxides prepared. The other sulfated metal oxides were prepared using similar conditions as that of zirconia. We have also optimized the synthesis of sulfated tin oxide, since tin is the only metal with a nuclear magnetic resonance active nuclei of the five metal oxides known to become superacidic upon sulfation. Nuclear magnetic resonance analyses have enhanced our understanding of the bulk structure of these materials, the position of the sulfate group, and the location of protons which have been indicated by the presence of Bronsted acidity. Cross polarization and magic-angle spinning magnetic resonance techniques were used for the direct observation of surface metal sites, while different proton sites were distinguished by solid-state 1H CRAMPS, variable temperature T1 inversion recovery, and saturation recovery studies.

Sulfated zirconia prepared by a modification of the PNL derived Rapid Thermal Decomposition of precursors in Solution (RTDS) process proved to be both novel and successful. The resulting superacidic materials showed the highest catalytic activity of all sulfated metal oxides.

Presentations

T. D. Brewer. 1994. "Cooperative Government/ Industrial Projects." Presented at the Worldwide Catalyst Industry Conference, Philadelphia, Pennsylvania (invited presentation).

T. D. Brewer. 1994. "Pillared Clays as Solid Acid Catalysts." Presented at Washington State University Chemical Engineering Seminar Program, Pullman, Washington.

T. D. Brewer, D. W. Matson, and J. G. Darab. 1995. "A Continuous Hydrothermal Process to Prepare Sulfated Zirconia Solid Acid Catalysts." To be presented at the Worldwide Solid Acid/Base Industry Conference, Houston, Texas (invited presentation).

T. D. Brewer, W. J. Thomson, R. Gore, and X. Li. 1994. "Synthesis and Calcining Effects on the Catalytic Activity of Sulfated Zirconia." Presented at the ACS National Meeting, San Diego, California.

Advanced Instrumentation Real-Time Acoustic Planar Imaging of Dense Slurries - RAPIDS

Alireza Shekarriz (Analytic Sciences and Engineering)

Project Description

Flows of concentrated suspensions or solid-liquid mixtures are commonly encountered in pharmaceutical, pulp and paper, polymer, petrochemical, and many other industries. Flows of such mixtures are often susceptible to settling, blockage, and bridging. Because there are usually an abundance of solid particles in the mixtures, up to 70% or so by volume, the use of optical diagnostics tools is nearly impossible. Qualitative and quantitative visualization of the flow field in process lines could aid quality assurance and process efficiency. In this project, a new technique based on an existing PNL technology was developed for imaging and visualization of optically opaque slurries. This technique was based on ultrasonic holography and it offers a planar imaging capability which is a unique and one-of-a-kind approach.

Technical Accomplishments

A fluidized bed setup was designed and images of the fluidized bed were captured at different fluidization conditions (concentration and particle size) for various acoustic source and reference conditions. Each image was then digitized and the ensemble average grayscale level and in turn the attenuation coefficient was calculated. Calibration curves were obtained from fluidized bed experiments for conversion of the local attenuation coefficient to local concentration. These figures revealed the feasibility of obtaining the concentration of a solid-liquid suspension even to the maximum packing level of the solid particles. The attenuation as a function of the concentration was found to be consistent with single transducer measurements of other investigators which indicates the linearity of the imaging system in response.

When the acquired video images revealed moving texture, such as the image of a suspension of paper pulp slurry, such motion was used to infer the velocity distribution by cross-correlation methods. At present, flow field reconstruction is carried out in post-processing, but real-time capabilities can be incorporated in the future with dedicated image processing.

Publication

A. Shekarriz. "Planar Ultrasonic Technique for Velocity and Concentration Measurement in Dense Slurries." *International Journal of Multiphase Flow* (submitted).

Presentations

A. Shekarriz. 1994. "Imaging of Opaque Slurries." Presented at the 1994 TAPPI International Environmental Conference and Exhibit, Portland, Oregon, April 18-20.

A. Shekarriz. 1994. "Acoustic Imaging of Dense Suspensions." An invited lecture at Washington State University, Pullman, Washington, April 20.

A. Shekarriz. 1994. "Real-time Acoustic Planar Imaging of Dense Suspensions (RAPIDS)." Presented at the 12th U.S. National Congress of Applied Mechanics, Seattle, Washington, June 26-July 1.

Analytical and Reaction Chemistry

Donald M. Camaioni, Steven C. Goheen, and Amit K. Sharma (Chemical Sciences)

Project Description

The goal of this project was to determine the key reaction intermediates/pathways that operate in a low temperature plasma reactor to destroy organic contaminants in water. This work was performed to develop analytical methods needed to enhance process performance and applicability as well as provide a fundamental understanding of the reaction chemistry and mechanisms.

This work supports an identified PNL capability in conversion processes and low temperature plasma. A low temperature plasma is produced when a strong electric field is established in a gas, causing the gas to partially ionize, forming a plasma. This mechanism can be used to create reactive conditions to destroy contaminants. In addition, the technology has a potentially much broader application in the area of synthesis (e.g., oxygenates for fuels) and electrocatalyzed processing for unique industrial processes.

Recently, the destruction of volatile organic contaminants using a variety of plasma-generating devices (microwave, silent discharge, and corona reactors) has received considerable attention. This technique is promising in terms of decontamination capabilities because treatment occurs near ambient temperature and pressure, requiring significantly lower energy and capital equipment costs than traditional thermal treatment. Chemicals successfully destroyed in plasma discharges include aliphatic hydrocarbons, benzene, toluene, methylene chloride, trichlorotrifluoroethane, and phosgene. PNL has already established a degree of practical capability in this area.

Technical Accomplishments

Since FY 1992, PNL staff have been studying a point-to-liquid plasma reactor. This technique employs a high-voltage direct current discharge between a negatively charged needle and an electrically grounded liquid, where the needle is the cathode and the liquid surface itself is the anode. Scouting experiments had shown that this technique was effective in destroying a wide range of liquid-phase organics, including organic dyes, EDTA and citric acid (two important contaminants in Hanford tank wastes), and carbon tetrachloride (a contaminant in Hanford groundwater). Subsequent work has been concerned with understanding its physical and chemical mechanisms of operation, assessing the potential for treating liquid wastes, and developing criteria for scaling up the process.

Experiments on the liquid corona phenomena have led to FY 1994 accomplishments in several areas.

Measurements of the number of solution phase oxidation per electron discharged duplicated the previous year's findings and explored effects of the ground electrode configuration and placement. Using iodometry, it was observed that a yield of 100 oxidations per electron discharged in a potassium iodide solution could be obtained with a circular grounding grid immersed in the liquid. This yield is 25% greater than the yield obtained using a wire ground immersed in the water and 180% greater than the yield obtained when the grid was placed between the point and the liquid.

Using an ultraviolet-vis spectrophotometer equipped with flow cells, the production of nitrate ions in distilled water and ozone in the headspace of a liquid corona reactor was confirmed and quantified (ozone in the reactor headspace was also detected in the flowing-after-glow mass spectrometer). The ozone concentration reaches a power-dependent steady-state concentration after several minutes of operation, while the nitrate concentration increases steadily with time. The concurrent production of protons manifested by a decrease in pH comparable to the nitrate produced establishes unambiguously that nitric acid is produced by the discharge. The initial yield of ozone was measured and ranged from 15 to 30 molecules per electron discharged depending on applied power and electrode configuration. Using the same reactor, iodometry measurements gave oxidation yields of 45 to 60 iodide ions oxidized per electron discharged. Considering that two iodide ions are oxidized by one molecule of ozone, these complementary results indicate that ozone is the dominant oxidant in the reactor. The nitric acid yield is small by comparison, less than 1 molecule per electron discharged. Experiments have been performed to measure the effects of power variations and electrode-to-ground surface distances and comparisons of yields with the ground electrode in water versus above the water. Although considerable scatter was observed in the data, yields of ozone by ultraviolet detection and oxidation events by iodometry were not strongly dependent on power for a given electrode-solution gap distance. However, yields appear to go through a maximum as the gap distance is varied (Figure 1). Considering that power consumption increases with the gap distance, a compromise may need to be reached between optimum oxidant production and power consumption.

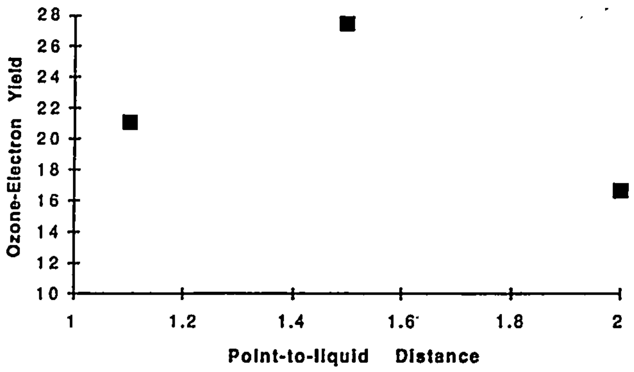


Figure 1. Ozone Yield Per Electron Discharged Versus Point-to-Liquid Distance. Points are an average of runs with currents at 15, 30, 45, and 60 μamps. Yields at each distance appeared to be independent of current within experimental errors.

Electron paramagnetic resonance spectroscopy spin-trapping experiments were performed by circulating the reactor solution through the spectrometer sample cavity. Signals for free radicals were observed from two different spin trapping agents (see Figure 2). The results suggest that degradation of organics involves radical pathways. A literature search of the reactions of ozone, oxygen-centered radicals, and oxygen atoms with the spin traps showed that some work had been published in this area. However, contradictions in the literature and the novelty of our experiments complicate the interpretation of the data.

Several experiments were performed to study the destruction of carbon tetrachloride dispersed in water. A sealed Pyrex glass vessel with an entry and exit port was constructed for this study. A 400 mL solution containing 100 μL of CCl_4 in the liquid phase were exposed to 14 to 17 KeV in a point to plane electrode configuration for 140 to 150 hours. Destruction was followed by periodically sampling the reactor head space gas and analyzing it by gas chromatography. Chloride and nitrate analyses were

Figure 2. EPR spectrum (100 gauss width) of spin-adduct formed by discharge of a solution of 10 vol% methanol in water containing 0.01 M pyridyl-*N*-oxide-*t*-butylnitrone.

also performed before and after the run to obtain a chlorine mass balance. Approximately 80% of the chlorine initially present in the CCl_4 was recovered as HCl. Some chlorine may be lost as Cl_2. A control experiment showed no significant formation of HCl when the discharge was not on. The other major product was carbon dioxide.

The kinetic data seems to suggest zero-order kinetics. Considering the long lifetimes of CCl_4 in this experiment and that a significant portion of CCl_4 is in the vapor phase due to its high volatility, its destruction may be taking place predominantly in the gas phase. In which case, it would be more efficient if carbon tetrachloride were sparged from the water and routed to PNL's gas phase plasma reactor.

Presentation

D. M. Camaioni, S. C. Goheen, and A. K. Sharma. 1994. "Treatment of Organic Contaminants in Water by a Corona Discharge Reactor." Presented at the First International Conference on Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, June 25-30.

Catalyst Development and Testing

Thomas D. Brewer (Materials Sciences)
Charles H. F. Peden (Materials and Interfaces)
William J. Thomson (Washington State University, Department of Chemical Engineering)

Project Description

The objective of this project was to develop and evaluate new catalytic materials for industrially important chemical reactions. The catalysts will be novel metal oxides synthesized by unique methods including Rapid Thermal Decomposition of precursors in Solution (RTDS), non-aqueous synthesis of mesoporous materials, and direct intercalation of oligomeric cations between clay layers. The catalysts will be evaluated for activity and selectivity for isomerization, alkylation, and methane coupling reactions.

It was also the goal of this project to develop the foundation for understanding the structural properties of the solid superacids which are giving rise to the unique and interesting chemistry observed in these systems.

Catalytic reforming is the second most important process for converting hydrocarbons in petroleum refining after catalytic cracking. Alkylation and transalkylation of aromatic compounds are processes well known for their ability to produce products such as ethylbenzene, cumene, and linear alkylbenzenes, that are in turn, important chemical precursors in the production of detergents and polymers. Alkylation catalysts that are known to produce alkylaromatic compounds include the commonly used Friedel-Crafts catalysts: sulfuric acid, phosphoric acid, hydrofluoric acid, and aluminum chloride. However, these catalysts typically produce undesirable byproducts such as oligomers and heavy polyaromatic compounds, as well as an extremely corrosive sludge byproduct.

There have been recent literature reports that amorphous zirconium, titanium, hafnium, iron, and tin oxides become superacidic after sulfation and subsequent thermal crystallization. Such superacidic catalysts hold great promise as replacements for the conventional Friedel-Crafts catalysts. Besides this application, sulfated superacidic oxides have shown great promise for a number of air-pollution control catalytic processes; notably, the removal of NOx from both stationary (power plants) and mobile (automobiles operating under "lean-burn" conditions) sources. As such, there is an opportunity to have a significant impact on the economy of a number of catalytic processes by the development of these materials.

Technical Accomplishments

Sulfated zirconia was found to be the most promising solid acid catalytic material. As a result of thermal and dynamic x-ray diffraction studies performed at Washington State University and Hammett indicator tests, zirconium oxyhydroxide appears to need a thermal pretreatment to remove water molecules adsorbed onto the surface before sulfation. The removal of water molecules facilitates handling and separation of the metal oxyhydroxide. However, the thermal pretreatment should not be of sufficient temperature or time to remove hydroxyl groups. If the hydroxyl groups are removed or condensed prior to sulfation, the metal oxide crystallizes and forms a stable phase which is resistant to sulfation. The resulting dehydroxylated materials, after sulfation, have proven to be ineffective n-butane isomerization catalysts. If the metal oxyhydroxide is thermally treated at a temperature and time sufficient to remove water but not hydroxyl groups, the resulting material can be sulfated with 0.5 to 1.0 molar sulfuric acid, followed by a final heat treatment which condenses the sulfate group onto the crystallized metal oxide lattice.

Hammett indicator studies were also used to determine the relative Bronsted acid strength of sulfated zirconia, as well as the relationship of Bronsted acidity to the final thermal treatment temperature of the sulfated oxyhydroxide. Sulfated zirconium oxyhyroxide was calcined in air at various temperatures for 3 hours, then allowed to cool to room temperature, followed by exposure to saturated water vapor for 96 hours. The samples were tested for Hammett acidity before and after exposure to water vapor using 2,4-dinitrofluorobenzene, which has a Hammett acidity of -14.52 (the Hammett acidity of 100% sulfuric acid is -12 and the scale is logarithmic, therefore this indicator tests for acid strengths greater than 100 times that of sulfuric acid). Samples calcined up to 450°C changed the color of the indicator both before and after exposure to water vapor, thus indicating strong Bronsted acidity, however, samples calcined between 475 and 600°C had no Bronsted acidity regardless of exposure to moisture. When the samples were calcined between 700 and 1000°C, the Bronsted acidity reappeared after exposure to water vapor. We believe that hydroxyl groups are present up to 450°C, which is the source of Bronsted acidity for these samples. Between 475 and 600°C, the hydroxyl groups have condensed to form water, and only Lewis acidity is present, which cannot be measured using Hammett indicators. Above 600°C, the samples regain Bronsted acidity after exposure to moisture due to the breaking of one of the two chelating bonds of sulfate to zirconia, thus producing a monodentate sulfate group, which can be protonated at the coordinatively unsaturated oxygen atom. This finding has far-reaching catalytic consequences, since we can now tailor the type of acid sites for a particular reaction using thermal treatment.

Thermal gravimetric analyses of uncalcined sulfated zirconia oxyhydroxides have indicated an initial weight loss due to the desorption of physically adsorbed water, followed by a second weight loss most likely due to dehydroxylation, with a third weight loss due to decomposition of the acid and liberation of sulfur trioxide. However, we believe that the decomposition of the sulfate group in sulfated zirconia is not complete, even up to 1000°C. It is possible that some of the sulfate is lost as sulfur trioxide, while a second type of sulfate only has one of the two chelating bonds broken. This could explain the presence of Bronsted acidity of samples after calcination at temperatures above the level for both dehydroxylation and decomposition of a single sulfate bond, followed by rehydration. Thermal gravimetric analyses of samples precalcined to produce crystalline sulfated zirconia show only two weight losses, one corresponding to physisorbed water and one corresponding to sulfate decomposition.

Hydroxyl stretching peaks can be observed using infrared analysis of a compressed Kbr pelletized sample of 2 wt% sulfated zirconia. FTIR studies have shown the presence of hydroxyl protons up to 450°C, but not at 475°C. Therefore, the FTIR evidence correlates well with that of the Hammett indicator studies for the presence of Bronsted acidity with respect to thermal treatment temperature. In addition, FTIR analyses of sulfated zirconia samples have revealed that the sulfate anion initially coordinates to the metal oxide surface in a bidentate, or metal oxide bridging, mode. As the final heat treatment temperature increases, the bridging bidentate peak gradually shifts to a chelating peak, which is the active form of the Lewis acid catalyst.

Sulfated zirconia catalytic materials have shown n-butane isomerization conversions between 57 and 45% over a 15 minute run at 200°C and a 0.2 minute residence time. For comparison, a commercially supplied sulfated zirconia catalyst showed between 60 and 34% conversion using the same reaction conditions. Samples calcined at 500°C were active isomerization catalysts; however, samples calcined at lower temperatures had decreasing activity. It appears that n-butane isomerization is catalyzed by Lewis acid sites; however, strong Bronsted acid sites may be necessary for other reactions.

Sulfated zirconia's catalytic activity results show it to be the superior n-butane isomerization catalyst of the five sulfated metal oxides prepared. The other sulfated metal oxides were prepared using similar conditions as that of zirconia. We have also optimized the synthesis of sulfated tin oxide, since tin is the only metal with a nuclear magnetic resonance active nuclei of the five metal oxides known to become superacidic upon sulfation. Nuclear magnetic resonance analyses have enhanced our understanding of the bulk structure of these materials, the position of the sulfate group, and the location of protons which have been indicated by the presence of Bronsted acidity. Cross polarization and magic-angle spinning magnetic resonance techniques were used for the direct observation of surface metal sites, while different proton sites were distinguished by solid state 1H CRAMPS, variable temperature T1 inversion recovery, and saturation recovery studies.

We have recently modified a PNL hydrothermal flow-through process which produces nanoscale materials into a process which can also produce superacidic sulfated zirconia catalysts. The Rapid Thermal Decomposition of precursors in Solution (RTDS) process uses hot, pressurized water at hydrothermal conditions to hydrolyze and oxidize metal ions present in solution and precipitates insoluble solid particles. Superacidic catalytic materials can be prepared using an additive in the precursor solution, while process optimization has included the necessity of reaction temperatures between 345 and 400°C. Catalysts produced by the RTDS process show isomerization activity comparable to catalysts produced by the more traditional base catalyzed precipitation method. Advantages of the RTDS process include the ability to produce metal doped sulfated zirconia in a single step, scaleability, and the formation of uniformly sized crystallites.

Publication

T. D. Brewer, R. Gore, and W. Thomson. 1994. "Sulfated Zirconia Solid Acid Catalysts." *Proceedings of the ACS National Meeting*, San Diego, California.

Presentation

T. D. Brewer, R. Gore, and W. Thomson. 1994. "Sulfated Zirconia Solid Acid Catalysts." Presented at the ACS National Meeting, San Diego, California.

Ceramic Permeation Membranes

Glenn W. Hollenberg (Process Technology and Engineered Systems)

Project Description

The purpose of this activity was to 1) investigate the unique separation characteristics of sodium fast ion conductors and 2) investigate the specific problem of contaminated sodium metal cleanup from liquid metal cooled reactors. These reactors (i.e., FERMI, EBR-I, EBR-II, and FFTF) possess(ed) metallic sodium as a coolant which is a mixed waste stream. The technical approach was to conduct sodium ions through beta-alumina membranes. These membranes do not permit other cations (i.e., cesium, strontium, aluminum, plutonium, etc.) to be conducted.

The goal was to provide data which verifies the ion selective character of ceramic membranes for separating sodium from radionuclides. The scope is limited to the operation of a high-temperature ceramic membrane in order to electrorefine sodium contaminated with cesium. Expected results are that pure sodium will be produced and that the cesium will be concentrated in the original feedstock. Decontamination factors as high as 10^5 are anticipated.

Technical Accomplishments

Two experimental accomplishments were completed during FY 1994: 1) construction of a metallic sodium cell and 2) execution of permeation (i.e., electrorefining) runs to produce clean sodium. Residual cesium in the electrorefined sodium was not measured because of the closure of the 325 Building.

Three beta-alumina tubes for electrorefining were obtained from commercial sodium-sulfur battery suppliers. In a inert gas glove box, a electrorefining cell was constructed consisting of a sodium melting vessel, the beta-alumina tube, and an electrochemical control circuit (i.e., galvanostat). Sodium doped with 2000 ppm cesium was synthesized as the feed material. (See the photograph.)

Two electrorefining runs were conducted; one at 260°C and another at 350°C. The galvanostat controlled the current to 1 amp which is equivalent to an ionic transport rate of sodium of 1 cc/hr. Approximately 10 cc of refined sodium was transported through the beta-alumina ceramic tube in a run. Literature data indicated that the decontamination factor (i.e., separation factor) should be better at 260°C.

Chemical analysis was not conducted because of the closure of the 325 Building facilities normally used for these measurements. The anticipated measurements would have provided relative cesium and sodium transport rates in the beta-alumina membrane which could then be used as the basis for separation factors.

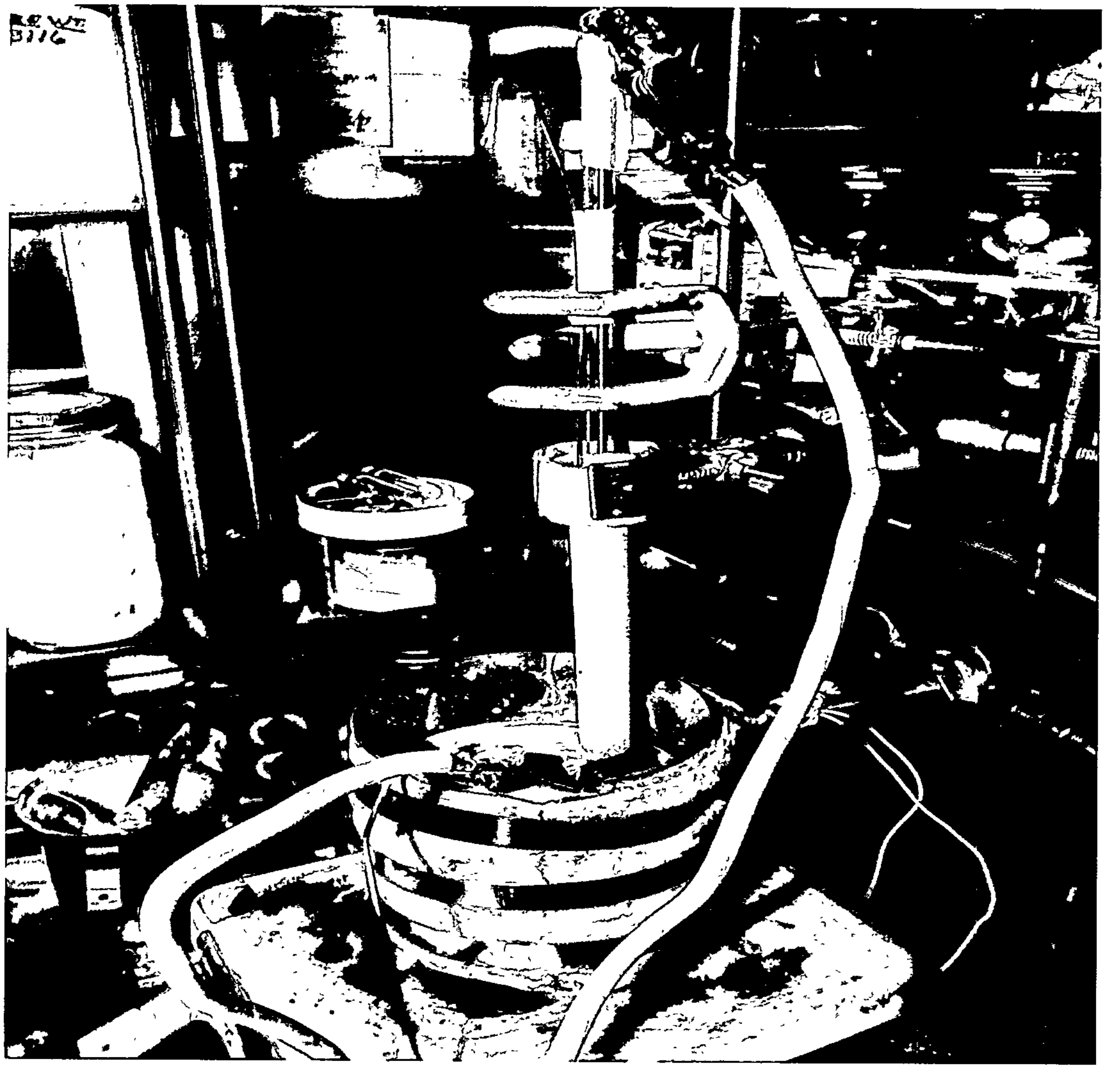
Extrapolation of these studies to an alternate sodium ion conductor, NASICON, provides the basis for aqueous separation of sodium. Interactions with industrial suppliers (Ceramatec Inc.) have demonstrated the ability of NASICON for salt splitting applications.

Publication

G. Hollenberg, C. Carlson, A. Virkar, J. Gordon, and A. Joshi. 1994. "Salt Splitting of Sodium-dominated Radioactive Waste Using Ceramic Membranes." In *Proceedings of SPECTRUM '94, Nuclear and Hazardous Waste Management International Topical Meeting.*

Presentation

G. E. Youngblood, D. J. Senor, D. Baldwin, and G. Hollenberg. 1994. "Electrochemical Refining/Separation of Sodium Using Solid Membrane Na-beta alumina and NASICON." Presented at the Electrochemical Society Meeting, Richland, Washington.



Solid Electrolyte Sodium Separation

Coatings Characterization

Gordon L. Graff and Jun Liu (Materials Sciences)

Project Description

The primary goal of this research was to develop a coatings characterization capability to thoroughly characterize the optical, magnetic, electronic, mechanical, and chemical properties of thin films and coatings.

Technical Accomplishments

Since the deposition rates for our biomimetic films were extremely slow, both Raman spectroscopy and transmission electron microscopy (TEM) were used to determine the fundamental mechanisms controlling film growth. Raman was used to monitor the hydrolysis and condensation reactions occurring in the deposition solutions while transmission electron microscopy was used to characterize precipitates in solution along with the deposited films. Raman spectroscopy showed that the Sn^{4+} ions in solution were undergoing rapid hydrolysis and precipitation. The transmission electron microscopy performed on solution precipitates confirmed that particle formation occurred by a nucleation burst (approximately 5 nm diameter particle size) with little or no subsequent particle growth. The transmission electron microscopy studies further showed that the thin film growth mechanisms are fundamentally different on polymeric (plastic) substrates than on SAM-containing metal substrates. This information was critical to further development of ceramic coatings for plastic substrate materials.

Jun Liu, a resident expert in materials characterization using transmission electron microscopy, joined the effort in FY 1994. His talents have proved invaluable in determining detailed chemical, structural, and growth mechanisms occurring in the synthesized thin films.

An automated, Dynamic Contact Angle measuring system was purchased using non-LDRD funds and added to the Coatings Characterization laboratory in FY 1994. This device enabled rapid measurement of substrate surface energies using contact wetting angle. This information is critical to understanding the effect of surface modification schemes on resulting thin film growth.

Computer Modeling of the Rheology of Dense Suspensions

David R. Rector (Analytical Sciences and Engineering)

Project Description

The objective of this project was to develop a "Stokesian dynamics" model to evaluate its usefulness in describing the rheological behavior of dense colloidal suspensions.

The transport and processing of dense suspensions of particles represents a major component of several activities currently under way at Hanford and PNL. Currently, the only means available to obtain rheological properties is from experimental data under very specific conditions or crude analytical models which have limited application for high concentrations. A computational method, known as "Stokesian dynamics," has recently been developed which simulates the behavior of many solid particles suspended or dispersed in a fluid medium. A simple "Stokesian dynamics" model is developed and a calculation involving a limited number of particles is performed. The method is evaluated with respect to its usefulness in predicting the rheological behavior of dense colloidal suspensions.

Technical Accomplishments

A simple "Stokesian dynamics" computer program was developed and demonstrated. A computer program was written to generate mobility and resistance functions, which are required input to describe the hydrodynamic interactions between particles, for uniform spherical particles. The usefulness of the Stokesian dynamics code was demonstrated by obtaining results for two problems of practical interest. The first was predicting the viscosity of a particulate suspension as a function of solids concentration. The second was the prediction of hindered settling velocity as a function of solids concentration.

A report summarizing the methodology and results was prepared. As a result of this work, a colloids modeling project was created a part of the Tank Science Program.

Decontamination and Remediation of Metallic Process Components by Electrical Heating

Steven R. Billingsley (Process Technology and Engineered Systems)

Project Description

The primary focus of this project was to conduct a bench-scale feasibility analysis via a bench-scale test on an ohmic heating device that can be used to decontaminate underground piping. After the best concept for such a device was determined, a bench-scale test was implemented, which resulted in the successful heating of both carbon steel and stainless steel pipes through induction heating.

DOE currently has hundreds of miles of inactive metallic underground transfer lines for radioactive and chemical solutions and slurries (e.g., there are nearly 12 miles of underground metallic piping within the 100 Area of the Hanford Site). These pipelines exist under roads, adjacent to operating facilities, at various depths, and various stages of deterioration. The current baseline remediation technology involves excavation and disposal of these inactive lines which entails significant cost and disturbance of existing operations. Because of their past use, internal radioactive and chemical contamination in the pipelines make them hazardous and expensive to remove for treatment and disposal. Application of an in situ remediation technology would allow for a reduction in the cost and complexity of remediation of these transfer lines.

Documentation on the Hanford area underground process lines, sewer lines, and transfer lines is incomplete, and is in the process of being compiled by Westinghouse Hanford Company in support of the Hanford Area Geographic Information System (GIS). Geographic Information System project personnel indicate that much data does not become available until construction crews encounter these lines. As a result, work activities are ceased while the line is assessed for potential contamination. The chemical process lines in the 200 Area processing facilities and tank farms are the best documented as to pipeline construction materials. Materials are generally carbon steel, black steel, and stainless steel; and many lines consist of a pipe within a pipe. The majority of chemical process lines are 2-inch, 3-inch, and 4-inch internal diameter pipes, with the largest percentage consisting of 3-inch. Sewer lines can be 6-inch diameter and larger. The newer lines are sealed on the exterior with polyurethane that is held away from the line with a bubble-pack material. Process lines have been actively cathodically protected against external corrosion since 1947.

Technical Accomplishments

After study of potentially applicable electrical techniques, the induction technique was chosen. Resistance (or ohmic) heating was eliminated because it uses the pipeline as part of the circuit. The resistance heating technique consists of leads being connected to each end of the pipe and applying current. The internal resistance of the pipe to the current will cause the temperature of the pipe to increase, and as the metal pipe is heated, the resistance increases, allowing for further heating. However, imperfections, cracks, flanges, or turns in the pipeline will generally have more initial resistance to current than the other portions of the pipe. This results in these sections being heated more rapidly, and developing hot spots. If these become hot enough to melt, the circuit will be broken.

With the induction technique, the heating can be much more uniform, as it relies only on the internal resistance of the material being heated. Induction heating has been in industrial use for several decades. In the last decade, computer modeling studies of induction heating have taken place. These include studies on ferromagnetic piping and noncylindrical geometries. The technology typically uses insulated copper induction coils wound into a cylindrical geometry. When the energized coil is placed closely to a conductive material, electromagnetically induced eddy currents form within the material, rapidly heating the material via the internal resistance of the conductive material. The cylindrical geometry of the coil causes the magnetic field to be most concentrated in the interior of the coil. However, induction coils can be designed to heat components of odd geometries. Induction heating coils have been designed for a number of purposes and can be used with a high degree of specificity. As the frequency of the alternating current is increased (250 kHz), the heating becomes a more surficial phenomenon. This surficial heating necessitated emplacing the coil in the interior of the pipeline. Because the magnetic field is not as concentrated on the exterior of the induction coil as on the interior, it was determined that bench-scale testing of the internal induction coil was necessary. The proof-of-principle test was designed to show that internally heating a pipeline by induction was sufficient to volatilize contaminants from the surface of the pipe.

A bench-scale apparatus was designed to simulate an underground pipeline. A galvanized trough had holes cut into each end, and pipeline was inserted. The pipe was instrumented with internal and external thermocouples (thin-wired to avoid magnetic coupling), and the trough was filled with clean Hanford soil. Hollow copper tubing was wound into a 10-turn induction coil (5 inches long and 2.5-inch external diameter). This coil was powered by a 25 kW water-cooled induction heater. Carbon steel pipe (3-inch internal diameter) was heated to 300°C at a power output of 4 kW, in a period of 4.25 minutes. Stainless steel pipe was also tested, as this material is less efficiently magnetically coupled than carbon steel, and it also represents a large fraction of Hanford underground pipelines. It was demonstrated that at a power of 22.5 kW, 3-inch internal diameter 304L stainless steel pipe could be heated to 200°C in 1.33 minutes. It was also shown that the stainless steel pipe could be heated to 700°C, which indicates that the induction heating technique may be effective in fixing contamination to the surface of the pipe as well as removing contaminants via volatilization.

The success of the induction technique in heating pipelines internally is an indication of its potential usefulness as an in situ remediation technique. Subsequent activities would include testing the ability to fix contaminants to the surface of the pipe, combining the induction technique with chemical techniques to remove contamination or reduce radioactive activity within pipelines, and design of a field-deployable system.

Development of a Selective Solid TRU Extractant

Brian M. Rapko (Chemical Technology)

Project Description

Currently, the baseline technology in the U.S. for removal of transuranic elements is the TRUEX (transuranium extraction) process. A carbamoyl-methylphosphine oxide is used as the extractant in the TRUEX process, which is a liquid-liquid extraction system for the selective removal of transuranic elements from acidic, aqueous radioactive waste streams. This project involved modifying the compound's structure with the final goal of incorporating the extractant through direct, covalent, carbon-carbon bonding into a polymer framework.

This project was divided into several sections. The first section involved synthesizing and characterizing a number of potential polymer precursors, as well as an additional series of model compounds. These model compounds are needed to assess the impact of the structural modifications necessary to covalently incorporate the extractant into a polymer with the modified compound's ability to extract transuranic elements. The second section involved evaluating the modified compound's ability to extract transuranic elements as a function of nitric acid concentration. The third section involved the preparation and characterization of polymers containing the transuranic element extractant. The fourth and final section involved evaluating the polymer's ability to extract transuranic elements in a solid-liquid system with the model extractants in a liquid-liquid system.

Technical Accomplishments

During FY 1993, the first section was completed. Two classes of transuranic element-selective extractants were modified to incorporate a polymerizable functionality. The same approach was used to prepare model compounds with similar steric and electronic properties. This work demonstrated that the polymer precursors could be prepared in good yield and with a high degree of purity. During FY 1993, investigations began to evaluate the effects of these modified compounds' ability to extract transuranic elements. As a result of this work, judgments on how such manipulations will affect the transuranic element extraction behavior of the product can be made now with some confidence.

In FY 1994, repetition of several of the transuranic element distribution measurements enhanced the precision and verified the accuracy of the data. In addition, the range of model compounds prepared was expanded (see Figures 1 and 2). Various aspects of this work were presented in two widely attended public meetings.

In collaboration with Dr. David Nelson of PNL, experiments focused on incorporating these modified transuranic element extractants into a solid polymer began. Both free radical and Ziegler Natta methods of polymerization of a variety of the modified transuranic element extractants with copolymers were examined. Surprisingly, in most instances, no incorporation of these modified transuranic element extractant was observed. In several cases, indirect evidence exists for polymers containing the transuranic element extractant. Unfortunately, as these materials were highly viscous oils, the physical properties of these materials are undesirable for the target transuranic element extractant system. The most recent experiment conducted in FY 1994 produced a solid material where indirect evidence exists for a polymeric product containing the transuranic element extractant.

The synthesis and characterization of these modified transuranic element extractants was accomplished. The modified compounds retain the ability to extract such transuranic elements as Am^{3+}, Pu^{4+}, and UO_2^{2+} from aqueous nitrate solutions in a liquid-liquid extraction system. Experimental work on incorporating these compounds into a solid polymer began. Preliminary studies indicate that the preparation of a solid polymer containing the transuranic element extractant was successful. Various aspects of the liquid-liquid extraction studies have been presented in two public presentations and a paper based on the transuranic element extraction properties of the model compounds has been submitted as an invited contribution to a book on separations of f-elements.

Publication

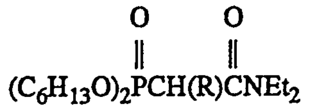
B. M. Rapko. "Synthesis, Characterization and Actinide Extraction Behavior of Bridge-Modified Carbamoylmethyl-Phosphonates and -Phosphine Oxides" in Advances in F-Element Separations, Plenum Press, New York (in press).

Presentations

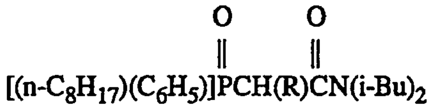
B. Rapko. 1994. "TRU Extraction by Bridge-Modified Carbamoylmethyl-Phosphonates and -Phosphine Oxides." Presented at the 207th National Meeting of the American Chemical Society, San Diego, California, March 13-17.

B. Rapko. 1994. "TRU Extraction by Bridge-Modified Carbamoylmethyl-Phosphonates and -Phosphine Oxides." Presented at the 18th Actinide Separations Conference, Durango, Colorado, May 23-26.

Prepared Compounds:

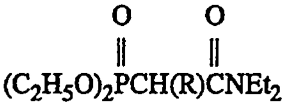


$(C_6H_{13}O)_2P(=O)CH(R)C(=O)NEt_2$



$[(n\text{-}C_8H_{17})(C_6H_5)]P(=O)CH(R)C(=O)N(i\text{-}Bu)_2$

	$(C_6H_{13}O)_2PCH(R)CNEt_2$		Yield	$[(n\text{-}C_8H_{17})(C_6H_5)]PCH(R)CN(i\text{-}Bu)_2$		Yield
R=	$CH_2CH(CH_3)_2$	(Isobutyl)	80%	$CH_2CH(CH_3)_2$	(Isobutyl)	89%
	$(CH_2)_7CH_3$	(Octyl)	95%	$(CH_2)_7CH_3$	(Octyl)	97%
	$(CH_2)_6CH=CH_2$	(1-octene)	73%	$(CH_2)_6CH=CH_2$	(1-octene)	100%
	$CH_2CH=CH_2$	(Allyl)	100%	$CH_2CH=CH_2$	(Allyl)	100%



$(C_2H_5O)_2P(=O)CH(R)C(=O)NEt_2$

R= $(CH_2)_7CH_3$ (octyl) 74%

Characterization:

- NMR [^1H, $^{13}C(^1H)$, $^{31}P(^1H)$] Spectroscopy
- IR Spectroscopy
- Chromatography - GC, TLC
- Mass Spectroscopy
- Extraction Behaviour

Figure 1. Prepared and Characterized Compounds to Date

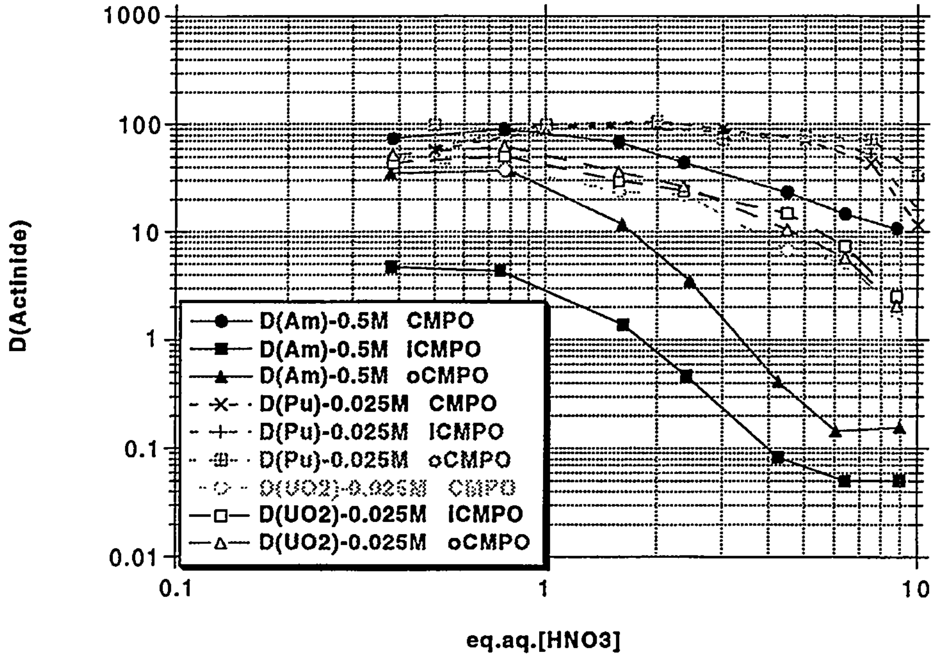


Figure 2. Summary of Actinide Distribution Values (D) with CMPOs

Diamond-Like Carbon Coatings

Edward L. Courtright (Materials Sciences)

Project Description

This project was directed toward the development of thermal control glazings for window applications (e.g., buildings or automobiles). Thermal control glazings produced by the polymer multilayer technology under development at PNL offers the potential for retrofitting existing windows with a cost-effective solar control coating. The end objective was to produce a roll of very thin gauge optically clear material that could be laminated to window surfaces. These glazings require a hard, durable coating to protect against dust, condensed moisture, household chemicals, fingerprints, and abrasive cleaning practices. Thus, the development of an optically clear diamond-like carbon coating would provide the enabling technology necessary to make this concept work.

Technical Accomplishments

A small laboratory coater setup was configured to produce preliminary diamond-like carbon coatings. Acetylene diluted with hydrogen was used as the precursor gas. Several hard coatings were successfully applied to a variety of plastic substrates. The hardest coatings were produced at a low hydrogen dilution, but were optically opaque. Optically transparent coatings with a light brown hue were produced with higher fractions of hydrogen and applied successfully to several sets of polycarbonate safety lenses. These coatings were hard enough to resist abrasion with a number 2 eraser consisting of aluminum oxides particulates in a rubber binder. These erasers readily scratch and degrade conventional polycarbonate lens surfaces. The coated safety glasses, which look like a high quality sunglass, have been featured in a number of tours and demonstrations.

The next step was to add oxygen to the hydrogen/hydrocarbon gas mixture to help destroy the graphitic sp^2 bonding and promote the desired tetrahedral sp^3 structure. Since hydrogen and oxygen are potentially explosive, a safety review was conducted to ensure that the coatings could be deposited in a safe manner.

Dual-Gas Tracer Characterization of Diffusion Limitations in Enhanced In Situ Remediation

Phillip A. Gauglitz, Loni M. Peurrung, and Gautam Pillay (Process Technology and Engineered Systems)

Project Description

Effective design of in situ remediation technologies often requires an understanding of the mass transfer limitations that control the removal of contaminants from the soil. In addition, the presence of nonaqueous phase liquids (NAPLs) in soils will affect the ultimate success or failure of remediation processes. Knowing the location of NAPLs within the subsurface is critical to designing the most effective remediation approach. This work focuses on demonstrating the ability of gas tracers to detect the location of the NAPLs in the subsurface and to elucidate the mass transfer limitations associated with the removal of contaminants from soils.

Soil and groundwater contaminated with organic compounds, such as carbon tetrachloride, trichloroethylene, perchloroethylene, machine oil, and gasoline, are widespread in both the government and private sectors. Attempts to clean up these toxins can be less successful than predicted because the presence of NAPL was not detected, the NAPL could not be effectively located, and/or mass transfer limitations slowed the remediation. Locating both NAPLs and dense nonaqueous phase liquids (DNAPLs) in the subsurface has been very difficult historically. Often the only way to know that a NAPL/ DNAPL is present is for a noticeable oil phase to appear in wells. However, wells sample an exceeding small volume of the soil, making them an impractical method for locating NAPLs when they are expensive to drill. Moreover, the distribution of the NAPL/DNAPLs as either isolated droplets surrounded by water or as spreading films affects both the removal of the NAPL/DNAPLs from the soils and their migration in the subsurface. Therefore, a method for determining the location, size, and nature of these organic phases is a critical need in the area of environmental remediation.

Injecting and extracting tracers from adjacent wells offers a technique for sampling the large volume of soil between the wells. Tracer tests have been applied widely for understanding the distribution of gas and liquid flow in soils and porous media, and partitioning tracer tests have been extensively used to estimate crude oil saturation in oil reservoirs, which is analogous to NAPL detection in an aquifer. However, only very recently have researchers attempted to detect NAPL/DNAPLs in unsaturated soils with partitioning gas tracers.

When gas tracers with different solubilities in water and NAPL phases flow through contaminated soils, the tracers will propagate at different velocities depending on the relative partitioning of the tracers into the water and NAPL. The dual-gas tracer technique seeks to exploit these different rates of propagation. By selecting tracers that partition, or dissolve, selectively into the phases of interest, the relative rates of tracer transport can be used to infer quantitative information about the amount, location, and relative geometry of those phases. Methods based on the relative solubility of tracers, such as the proposed method, are commonly referred to as partitioning tracer methods.

To detect NAPL/DNAPLs, two tracer gases, which are identical except for their solubility in the NAPL/DNAPL, are injected into the soil. By analyzing the difference between the two tracers as they leave the soil, the existence and amount of the NAPL/DNAPL can be determined. Understanding the location and amount of NAPL/DNAPLs within soils will allow for an optimal placement of wells for remediation or, equivalently, will allow for the minimum number of wells for effective remediation. In both cases, determining the location and amount of NAPL/DNAPLs within soils will greatly reduce the cost of remediation. For advanced remediation processes, the success and cost effectiveness often hinge on whether the rate of removal of underground contaminants will be limited by the contaminants' volatility or by slow diffusion processes. The difference in the elution of the two tracer gases from the soil also highlights the critical diffusion limitations within the soil. This information can then be used to select and properly design the most cost-effective remediation method.

Partitioning gas tracers for detecting NAPL/DNAPLs offer a cost-effective technique for sampling a large volume of soil. Because tracers are generally confined to the region between points of injection and withdrawal, a partitioning tracer method will only give a positive detection if the NAPL/DNAPLs occur between these two wells. Accordingly, by injecting the partitioning tracers in multiple wells surrounding the region of NAPL/DNAPL contamination, the spatial location of the NAPL/DNAPLs can be determined.

Technical Accomplishments

In FY 1994, proof-of-concept experiments were completed to demonstrate the retention of tracer gases in soils with a range of NAPL and water contents. A suite of fluorinated gases with a wide range of solubilities were tested as tracers. These tracers, including SF_6, C_2F_6, C_2F_4, and CHF_3, are detectable at very low concentrations (as low as parts per billion) using a gas chromatograph with an electron capture detector. The solubility of the tracers in both the NAPL/DNAPL and the water phases within the soil directly affects the retention of the tracers.

Tracer retention experiments with NAPL saturations of 0, 2.1, 4.2, and 6.3% showed that the retention of a NAPL-soluble tracer increased monotonically with the amount of NAPL in a sandy soil. As expected, insoluble tracers were unaffected by the presence of the NAPL. In these proof-of-concept experiments, mineral oil was used as the NAPL phase and trichloroethylene was used as the NAPL-soluble tracer. Fluorinated gases that should be more suitable as NAPL-soluble tracers were identified and purchased, but not tested.

Computer simulations of the retention of soluble and insoluble tracers were performed and confirmed that NAPLs retain soluble tracers. These computer calculations used an assumption of local equilibrium between the tracers and the NAPL; this assumption neglects mass transfer limitations. Comparison of the experimental and theoretical results highlighted a distinct feature in the experimental results that was absent in the modeling results. This feature, a long, tailing tracer elution from the soil, is a result of mass transfer limitations within the soil. Thus, the dual-gas tracer technique offers information on the nature and extent of these mass transfer limitations. However, future work will require a model that can account for such limitations.

Electric Field and Current Modeling of Electric Discharge Processing

Delbert L. Lessor (Analytic Sciences and Engineering)

Project Description

The high efficiency corona (HEC) reactor destroys molecular gaseous contaminants in a flow steam by an electrical discharge in a packed bed. In this project, the modeling effort was closely coordinated with experimental testing and development. Our purpose in modeling the high efficiency corona reactor was to aid in interpreting the observations and measurements, to aid in elucidating the physical phenomena, and to give insights for its optimization and scale-up.

Technical Accomplishments

The high efficiency corona reactor uses a power line frequency discharge across a packed bed of dielectric beads or granules in the cylindrical annulus region between a rod electrode of small radius and a coaxial dielectric barrier cylinder of larger radius. The second electrode is a foil or screen in contact with the outside surface of the dielectric barrier cylinder, so that the barrier serves to inhibit direct charge transfer and hence tends to behave as a capacitive element in series with the nonlinear circuit element of the bed discharge region. We believe, however, that the dielectric barrier region plays a number of roles in the operation of the bed, and that it is not necessarily a pure capacitance as a circuit element. The active region of the high efficiency corona is the annular packed bed region, where reactant species are produced and subsequent chemical reactions occur.

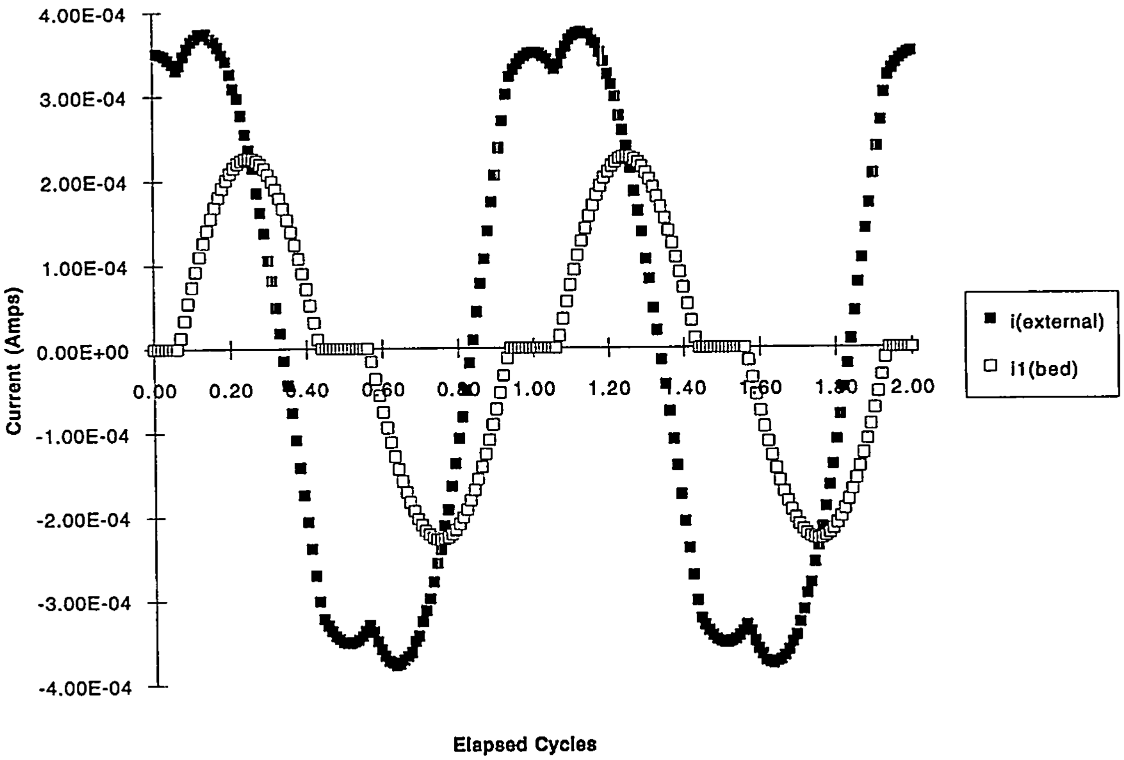
Features of the Model

A cylindrically symmetric time dependent model suitable for computation of transients through a few cycles of driving voltage was developed as a first tool in understanding the high efficiency corona reactor. The model takes into account the effects of charge accumulation on the inside surface of the dielectric barrier, though a higher-dimensional model would be necessary to adequately describe the effect of the dielectric barrier in suppressing streamers. The packed bed region is modeled as having most of its potential drop occur in the region without electron multiplication. Thus, the charge carriers are negative ions (from electron attachment) or positive ions (from ionization in the high field region) on the negative and positive half-cycles, respectively. Effects of the space charge of the charge carriers on the electric field is taken into account. This model for the packed bed region is similar to ones used to describe electrostatic precipitator discharges. The mobilities of the charges in the packed bed region are parameters whose fitting should give some insights on what is occurring there. A more detailed model for the packed bed region having ionization and attachment processes will be tested later.

Results of Modeling

The figure shows computed external current and current in the packed bed region, plotted as a function of time during two cycles of driving voltage in a startup transient. The onset of bed current at a threshold condition and its subsequent extinguishing by a combination of driving potential reduction and charge accumulation on the dielectric barrier are shown.

One insight from the modeling effort has been that the actual resistance of the dielectric barrier is probably not critical to the operation of the high efficiency corona reactor, provided that it does not permit arcing through and that the time constant for charge redistribution on the barrier is long compared with typical time duration of streamers. A fitting of the charge mobility parameters in the packed bed region to experimental voltage-versus-current information for a number of high efficiency corona reactor geometries is expected to give insights on whether the charge transfer in the packed bed region is ion motion in the spaces between granules or surface conduction on or within granules of the packed bed.



Calculated Currents in External and Packed Bed Regions of Reactor with 35 KV Applied

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Presentation

W. Heath, S. Barlow, T. Bergsman, D. Lessor, T. Orlando, A. Peurrung, and R. Shah. 1994. "Development and Analysis of High Energy Corona Process for Air Purification." Presented at the 1st International Conference on Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, Canada.

Evaluation and Selection of In-Well Separations

Thomas M. Brouns and Ward E. TeGrotenhuis (Process Technology and Engineered Systems)

Project Description

In-well treatment of groundwater contaminant plumes offers several advantages over conventional pump and treat scenarios, including reduced pumping and equipment costs, as well as ALARA (as low as reasonably achievable) and regulatory benefits. Currently, the technology is being applied to remediation of volatile organic contaminants through vapor stripping and bioremediation. The objective of this project was to determine the applicability of using multi-screened recirculating wells for the removal of metal and radionuclide contaminants. Critical issues addressed are the feasibility of potential in-well treatment processes, and the effectiveness of this approach at transporting contaminants from the aquifer into the well bore for treatment.

Technical Accomplishments

A serious problem throughout the DOE complex as well as private industry is groundwater plumes contaminated with heavy metals and radionuclides. The conventional strategy for treating groundwater plumes is pump and treat with multiple extraction wells or the combination of extraction and reinjection wells. Sorption of contaminants onto the aquifer matrix and migration into pore space not accessible by moving water causes long remediation times and multiple flushing to achieve cleanup. An innovative alternative to pump and treat is the use of multi-screened, recirculating wells. In these wells, groundwater is withdrawn from the aquifer into the well through a lower screened interval and reinjected at or above the water table through a second interval, thereby generating a recirculating flow through the aquifer.. The combination of extraction and reinjection within the same well provides the opportunity for treatment within the well bore, and avoids costly pumping of groundwater to the surface and extensive ex situ treatment facilities. In addition, the same water is used to repeatedly flush a given region, and prevents water from being drawn from uncontaminated regions into the contaminated zone. Other benefits include ALARA advantages, and avoiding regulatory permitting for reinjecting treated groundwater.

Accomplishments in this project include a survey of contaminant plumes in the DOE complex, focusing on those contaminated with metals and radionuclides, in order to identify and characterize potential sites for remediation with in-well processing. A second accomplishment was a study of conventional and innovative treatment technologies that are potentially implementable as in-well processes for treating metals and radionuclides. An innovative technology was selected as the most promising for in-well metals treatment, and an apparatus was conceptualized for the technology. Finally, flow field calculations were performed to characterize important parameters, range-of-influence, and treatment times of recirculation wells.

A survey of groundwater plumes around the DOE complex portrays how metals and radionuclides tend to sorb very strongly in an aquifer, restricting mobility and making removal by flushing slow and inefficient. Consequently, contaminant concentrations in the extracted groundwater tend to be low. In addition, the toxicity of most heavy metals and radionuclides requires treatment to very low levels to meet drinking water standards or other applicable or relevant and appropriate requirements. High concentrations of naturally occurring ions add to the challenge of effective treatment, because feasible technologies must have high selectivities in order to avoid producing copious secondary waste volumes. A final complication in treating radionuclides is the presence of naturally occurring nonradioactive isotopes, which are carried along with the contaminants. An example of a groundwater plume that embodies these difficulties is the 216-B-5 Reverse Well IRM plume in the 200 East Area of the DOE Hanford Site. Radioactive contaminants in the plume are ^{90}Sr, ^{137}Cs, and $^{239/240}$Pu at maximum measured concentrations of 5028, 1546, and 51 pCi/L, respectively, which correspond to a range of 10^{-3} to 10^{-5} ppb. Strontium, for example, has a partitioning coefficient of 20 mL/g, indicating significant sorption onto the aquifer matrix, and a drinking water standard of 8 pCi/L. In addition, calcium and magnesium are present in the groundwater at concentrations of 30 ppm and 10 ppm, respectively, and naturally occurring strontium is present at 150 ppb. Although, the natural strontium is much more concentrated than the contaminant, it is much more dilute than calcium and magnesium, which will be the primary competitors in treatment. The extremely low plume concentration and treatment objectives, the high degree of sorption, and the naturally occurring ions combine to form a difficult technical challenge to recover and treat contaminants.

Conventional technologies considered for in-well treatment included precipitation, ion exchange, and membrane separation. None of these technologies are promising for in-well treatment of groundwater plumes, such as the one described above, because they cannot typically treat to strict drinking water standard, and/or generate large secondary waste volumes. This point is illustrated for ion exchange in Figure 1, where the volume reduction factor, assuming regeneration, is plotted as a function of K_d for a resin. K_d for commercial ion exchange resins have been measure at about 100 for strontium in competition with calcium, so processing a million gallons of groundwater will produce 10,000 to 100,000 gallons of regenerant waste. The relatively poor performance is primarily due to naturally occurring co-ions, which will dominate the vast majority of exchange sites in the resins.

Innovative technologies are becoming available that are much more promising for in-well treatment of metals and radionuclides. Two promising innovations in precipitation are electrochemical precipitation and iron reduction technologies. However, the most promising innovative technology is superadsorbents, which have been tested under groundwater conditions, and have shown K_d values as high as 10^5 for strontium. Figure 1 shows that these superadsorbents can reduce waste volumes by factors as high as 100,000. These adsorbents are regenerable and can be contained in a small column as part of an apparatus that can be inserted into a well bore for treatment.

Flow field calculations were also performed to estimate range of influence and treatment times of recirculation wells. An analytical solution of Darcy's Law for recirculating flow in a homogeneous, infinite porous media was used to approximate a two-screen recirculation well. Figure 2 illustrates the range-of-influence of a recirculation well in an isotropic aquifer as the fraction of total flow remaining within a distance r of the well bore. The radius is nondimensionalized by the screen spacing, and the only other parameter is screen height, which has a negligible effect. An indication of treatment time can be discerned by calculating the length of time for fluid to travel along a streamline passing through a given value of r in Figure 2. Relative cycle time provides additional indication of range-of-influence. The 25% fractional flow streamline is 5 times faster than the 50% fractional flow streamline, while the 75% and 90% streamlines are almost 16 and 600 times slower, respectively. In conclusion, the effectiveness of recirculation wells as a treatment strategy depends strongly on the depth of the aquifer, which limits the range of influence by limiting the spacing of the screens, which in turn dictates the number of wells required to treat a given plume. Other factors to be explored further in future work are effects of sorption and desorption kinetics, and effects of heterogeneities. In-well treatment using multi-screen recirculation wells is a technically feasible strategy for treating groundwater plumes contaminated with metals and radionuclides.

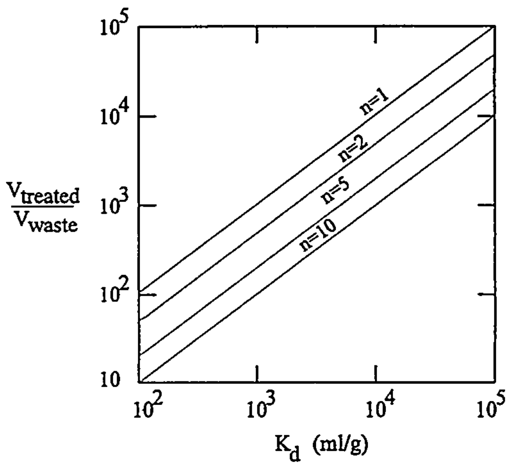


Figure 1. Ion exchange volume reduction factor as a function of partitioning coefficient, assuming n pore volumes to regenerate the exchange bed.

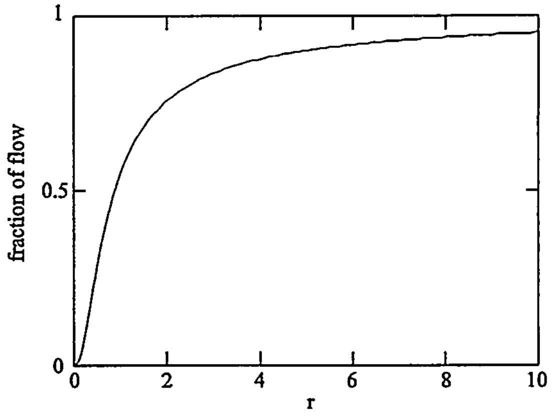


Figure 2. Fraction of the total flow recirculating through a two-screen well, that passes through a circle of radius r, centered at the well on a horizontal plane located half-way between the two screens; r is nondimensionalized by the screen spacing.

Experimental Investigation of Pipe Flows of Complex Fluids

John D. Hudson and Jon R. Phillips (Analytical Sciences and Engineering)

Project Description

An important but often ignored aspect of multiphase flow is the description of the particle phase behavior near a solid boundary. In FY 1993, an extensive review was conducted to clarify key technical issues in solid-liquid slurry flows. The review led to the initiation of fundamental experiments which consider the boundary interactions and turbulence in slurry pipe flows. The first of these experiments focused on obtaining velocity information of the dispersed phase near a pipe wall. The data was used to validate engineering codes and provide an experimental reference for analytical models.

Technical Accomplishments

A new experimental capability was developed in FY 1993-1994 which allows highly detailed measurements using optical techniques such as laser-doppler velocimetry and particle image velocimetry with refractive-index-matched slurries. Additional instrumentation provides pressure drop information, as well as control and monitoring of the system temperature. The facility includes a 25 m long, 2.5 cm polished stainless steel flow tube which will allow the study of laminar, transitional, and turbulent flows of slurries and complex fluids. The flows are driven by a four-stage progressing cavity pump capable of handling large particulates at high-volume fraction. System qualification is currently in progress.

The refractive-index-matched slurry used in the initial experiments will consist of solid acrylic particles in a liquid mixture containing a surfactant, a lubricant additive, and a halogenated hydrocarbon. This slurry provides an index match between the fluid, particulate, and test section with a density ratio which is tunable within a small range, affording experiments which require neutral buoyancy. In addition, this mixture is essentially non-flammable and has insignificant environmental impact when compared with other alternatives. Small quantities of the mixture have been prepared and transparency has been verified.

Publication

J. D. Hudson and J. R. Phillips. "Turbulence Production in Flow Near a Wavy Wall." *Experiments of Fluids Journal* (in revision).

Flash Evaporated Monomers

John D. Affinito (Materials Sciences)

Project Description

This project is a continuation of the polymer multilayer vacuum web coating development task. During FY 1994, the focus was on installation and testing of the polymer flash evaporation and electron beam curing systems that were fabricated under this project last year. The web coating system was used to test this new hardware. Monomer was flash evaporated with the flash evaporator system, condensed on the web substrate, and polymerized with the e-beam gun to form hard polymer layers.

Technical Accomplishments

Monomer Evaporation Process

The technique used to evaporate the monomer was to spray monomer fluid into a hot tube that has a very hot (i.e., the tube is hot enough to instantly vaporize the monomer spray, yet not hot enough to crack and/or polymerize the monomer on contact) pressure baffling, expansion nozzle on one end. Under these conditions the monomer evaporates as quickly as it is introduced into the tube—there is no pool of liquid in the tube. The baffles in the tube/nozzle system serve to build the pressure (of the molecular gas of monomer molecules) in the nozzle expansion chamber. Building the pressure serves to make the molecular gas stream, exiting the slit in the nozzle, more uniform across the length of the nozzle slit.

The flow of monomer into the hot tube is controlled with a precision metering pump. Dispersion with an ultrasonic atomizer yields the best layer thickness uniformity. However, 2% uniformity has been attained on capacitor runs, of several thousand layers, by just allowing the precision metered monomer flow to drip into the hot tube with the substrate moving past at 500 linear feet per minute.

Polymer Multilayer Deposition Systems

Figure 1 is a schematic of the vacuum web coater. The chamber is shown configured as it would be for depositing polymer/silver/polymer on polyester with the polymer multilayer process used in concert with sputtered silver.

The chamber in Figure 1 is set up in a modular fashion that permits multiple process enclosures to be mounted in any order for fabrication of multilayer structures. The current process capability includes polymer multilayer flash evaporation or monomer extrusion—with e-beam or ultraviolet cure; sputtering—reactive or nonreactive; crucible or rod fed e-beam evaporation—reactive or nonreactive; and plasma enhanced chemical vapor deposition. Further, the entire drum can be biased with radio frequency or direct current electric fields, any deposition source enclosure may contain radio frequency or direct current bias electrodes, and any combination of deposition zones can be biased with fixed or rotating magnetic fields. Also, radio frequency glow discharge cleaning can be applied to the substrate before, or after, any deposition zone via small modular enclosures.

Results of Polymer Multilayer/Silver Reflector Depositions

Figure 2 (left) shows the reflectivity curves for a polymer/silver repeated multilayer deposited on a polyester substrate and the reflectivity of silver sputtered directly onto a polyester substrate. The silver layers are 0.12 μm thick and the polymer layers are 1.5 μm thick. The leveling effect of the monomer/polymer layers can increase reflectivity by providing a much smoother surface. As well, the polymer layers serve to reduce pin holes in the metal film.

When the silver layer is made thinner (0.03 μm, Figure 2 right), multiple reflections are seen between successive polymer/silver cavities below the first surface of the multilayer stack. This permits the structure to act as a multiple cavity Fabry-Perot interference filter. Comparison of Figure 2 (right) with an optical model indicates that significant reflections are being returned from as deep as the fourth silver layer below the surface. This means that the three repeated peaks in Figure 2 (right) are higher order, resonant, transmission lines from a three-cavity Fabry-Perot interference filter.

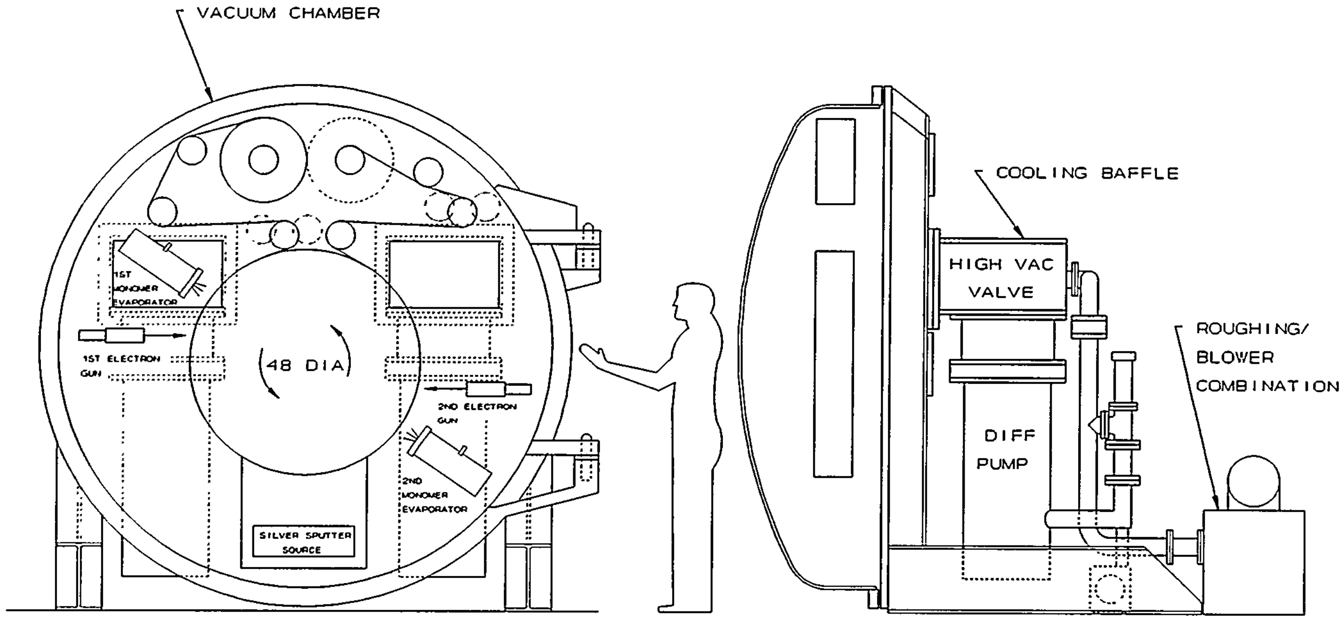


Figure 1. Schematic of PNL Deposition System

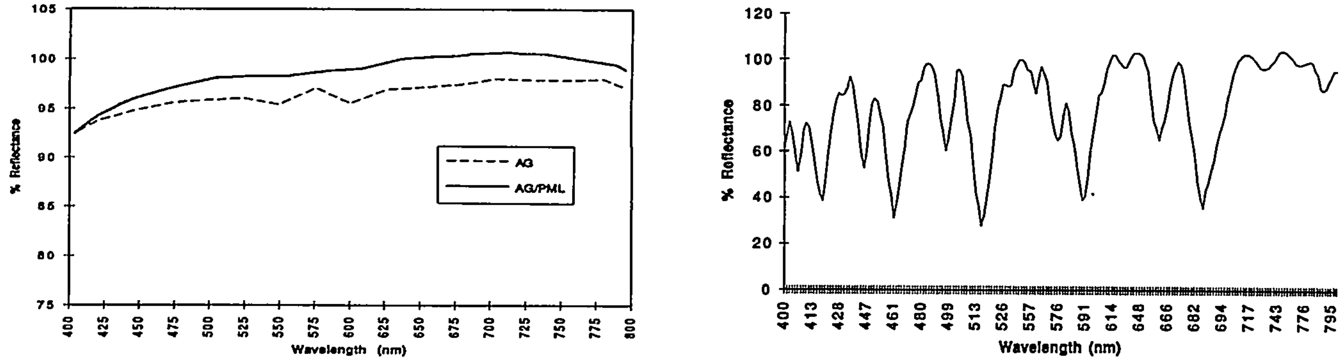


Figure 2. Left: Silver sputtered directly onto polyester (dashed line) and polymer multilayer silver repeated multilayer deposited on polyester. The silver layer is 0.12 μm thick in each case. Right: A polymer/silver (1.5 μm/0.03 μm) repeated multilayer. The reflectance spectra matches a model for a three-cavity Fabry-Perot interference filter.

Conclusion

Excellent reflectivity can be obtained from polymer/silver/polymer coatings vacuum deposited on polyester web. The reflectivity is significantly better than that obtained by direct deposit of silver onto the polyester substrate. The high rate and low absorption of polymer multilayer deposited polymer layers should permit a wide variety of optical interference type coatings to be deposited, in a cost-effective manner, on wide area flexible substrate.

Publications

J. Affinito, P. Martin, M. Gross, and W. Bennett. 1994. "Vacuum Deposited Polymer/Silver Reflector Material." SPIE Conference Proceedings - Optical Thin Films IV: New Developments, 276-283.

P. Martin, J. Affinito, M. Gross, and W. Bennett. 1994. "Coatings for Large-Area Low-Cost Solar Concentrators and Reflectors." SPIE Conference Proceedings - Optical Thin Films IV: New Developments, 217-222.

Fundamental Reaction Diagnostics/Kinetics

Stephan E. Barlow, Russell G. Tonkyn, and Thomas M. Orlando (Chemical Structure and Dynamics)

Project Description

Researchers at PNL have been developing high-energy corona reactors for the destruction of hydrocarbon contaminants. These reactors, which generate low-temperature plasmas and operate at atmospheric pressure, are potentially useful in large-scale remediation efforts. However, the details of the physical and chemical parameters which govern the destruction efficiency are, at present, poorly understood. We have developed a differentially pumped mass spectrometer system which can be used to sample virtually any plasma source. We have equipped this system with a Flowing-Afterglow and Chemical Ionization Source which allows us to sample selectively the neutrals present in the discharge region. This capability, when coupled with quadrupole mass spectrometry, allows us to sample the cation, anion, neutral, and electron number densities and hence "pick-apart" the plasma for detailed studies.

Technical Accomplishments

To date, we have utilized the Flowing-Afterglow Mass Spectrometer to probe the plasma parameters and plasma chemistry occurring in high-energy packed-bed coronas, which are used to destroy halogen containing hydrocarbon wastes, such as carbon tetrachloride. Work which addresses the specific role of the packing material in enhancing the destruction efficiencies has been carried out since surface-interface interactions and catalytic effects are expected to enhance destruction efficiencies. The catalytic packing materials were also investigated to determine their effect on byproduct generation. These tests demonstrated the near "real-time" monitoring capability of our new instrument. Soda lime bead packing materials were well characterized at various operating conditions. The results compared well with the data generated in a larger, laboratory-scale reactor and thus confirms the validity of the Flowing-Afterglow experimental results for predicting performance on larger scale prototypes. Two other catalytic materials, TiO_2 and ZrO_2, were also investigated on a preliminary basis. These materials showed significant improvement in destruction efficiency for CCl_4 and will be investigated further.

An important collaboration was established with Lawrence Livermore National Laboratories to investigate areas of common interest in corona processing technology. A PNL-designed reactor and power supply were shipped to LLNL facilities and tested using LLNL control and monitoring facilities. These tests examined destruction efficiencies of NO_x and a model hydrocarbon system such as C_3H_6. These tests were performed to assess the applicability of corona technology to cold-start issues in the automotive industry and also allowed PNL and LLNL to compare the relative merits of their respective corona technologies.

Homogeneous Isotropic Turbulence

Lucia M. Liljegren (Analytical Sciences and Engineering)

Project Description

The purpose of this research was to improve the understanding of turbulence in solid-liquid multiphase mixtures. Multiphase flows are frequently encountered at the Hanford Site and in many industrial applications. At Hanford, mixing, retrieval, transport, and separation of solid-liquid suspensions can benefit from this research. In industry, significant improvements in energy and chemical process efficiencies can be achieved by utilizing more accurate and experimentally verified physical models. Also, process equipment that handles multiphase turbulent flows can benefit from physically based design rules.

Improved understanding is achieved through two linked activities. The first is deriving rigorous transport models to predict fluctuating kinetic energy and the rate at which it is dissipated by viscous actions. The second is to obtain data which describes turbulence in a simple, well described flow field. Grid generated turbulence fits these conditions. Data from this flow field permits testing of models for the creation and dissipation of turbulence due to particle-fluid interactions. The data will then be used to verify existing turbulence models and assist in formulating new ones. Successful models will then be implemented in computational fluid dynamic codes such as TEMPEST.

Technical Accomplishments

Major accomplishments during FY 1994 fall into three categories: 1) completing development of a unique experimental test facility, 2) developing experimental techniques, and 3) performing analyses to develop turbulence models. A unique experimental facility to provide a homogeneous isotropic turbulence in a particulate mixture is now complete and operational. The facility was leak tested and retrofitted to ensure it could safely survive earthquakes. A method to measure dissipation of turbulent kinetic energy has been developed; this technique has been documented in Liljegren (1994). An index of an environmentally friendly refraction matched mixture which can be disposed of easily was obtained and will be used for the first phase of testing. In addition, the initial phases of testing the computational models for particulate flows have begun.

Additional details on accomplishments include the following:

- Completed a test section to allow measurement of fluctuating kinetic energy in both driven and self-induced turbulent flows. The test section was fabricated in FY 1993. Modifications were required to achieve stability during seismic events. The facility has been leak tested and is now operational.

- Developed an additional index of a refraction matched fluid-solid mixture to allow measurements using optical methods at high particle loadings. Two additional mixtures developed in past years are also available; these have special disposal needs. The mixture obtained this year is water based and can be disposed of using normal methods allowing more extensive testing.

- Tested a mixture model that predicts fluctuating kinetic energy in a gas-solid mixture. This mixture model was incorporated into TEMPEST and compared to published jet data. This work was done in collaboration with Hirr and Savery of Portland State University.

- Applied ensemble averaging to relate the dissipation rate to the fluctuating kinetic energy and the Taylor microscale in a particulate flow. This information is required to obtain a direct measurement of the dissipation rate in a solid-fluid multiphase mixture. Previously, this quantity could only be inferred from the decay rate of the fluctuating kinetic energy, and it was not possible to measure the separate contributions of viscous dissipation and dissipation or creation of fluctuating kinetic energy due to particle-fluid interactions.

- Documented and presented a derivation of the transport equation for fluctuating, or turbulent, kinetic energy in the continuous and discrete phase of a particulate mixture. This model was tested using data collected in experiments. This analysis was performed in collaboration with Foslein of University Wyoming; the analysis was completed September 1993.

Publications

L. M. Liljegren. 1994. "The Dissipation Rate of Fluctuating Kinetic Energy in a Fluid-Solid Flow." *Phys. Fluids* (in press).

L. M. Liljegren. 1994. "The Effect of a Mean-Fluid Velocity Gradient on the Particle-Fluid Velocity Covariance." *Int. J. Multiphase Flow 20 (5)*, pp. 969-977.

L. M. Liljegren. 1993. "Ensemble-Average Equations of Motion for the Continuous Phase of a Particulate Mixture." PNL-SA-23711, Pacific Northwest Laboratory, Richland, Washington, *J. Fluids Eng.* (submitted).

L. M. Liljegren. 1994. "The Ensemble Average Transport Equations for a Discrete Phase of a Particulate Mixture." PNL-SA-21173, Pacific Northwest Laboratory, Richland, Washington, *J. Fluids Eng.* (submitted).

L. M. Liljegren and W. Foslein. 1994. "The Fluctuating Kinetic Energy Budget for a Fluid-Solid Mixture." *Phys. Fluids* (submitted, currently responding to first cycle of referee comments).

Presentations

L. R. Hirr, C. W. Savery, and L. M. Liljegren. 1994. "Multiphase Turbulent Flow Model for TEMPEST: A Computational Fluid Dynamics Computer Code." Presented at the 12th National Congress of Theoretical and Applied Mechanics, BN-SA-3855 A.

L. M. Liljegren and W. Foslein. 1994. "Fluctuating Kinetic Energy in the Continuous Phase of a Particulate Mixture." Presented at the 12th National Congress of Theoretical and Applied Mechanics; also presented at the Portland State University seminar series.

Hydrogen Separation Technology Using the CHASP Process

Jagannadha R. Bontha and Jeff E. Surma (Process Technology and Engineered Systems)

Project Description

The CHASP process is a separation process developed by researchers at PNL for the treatment of enriched water. The process exploits the physical properties of enriched and proton water to achieve the desired separation. Although research is required to establish the cost-effectiveness of the CHASP process, initial estimates indicate that this process has several other potential applications in the field of waste water treatment.

The objective of this work was to demonstrate the effectiveness of the CHASP process for the recovery/removal of enriched water from waste mixtures of enriched and proton water. The scope of the work was to conduct proof-of-principle experiments to establish the capabilities of the CHASP process. It is expected that the CHASP process could become a cost-effective process for the recovery/removal of enriched water.

Technical Accomplishments

Equipment for the CHASP process was set up for nonradioactive material and experiments were performed with deuteriated water. Some preliminary data for the thermodynamic equilibrium conditions with deuterium oxide have been obtained. The preliminary results indicate that the thermodynamic conditions for the deuterium oxide are much different than those previously determined with proton water. More experiments are being conducted to determine the thermodynamic equilibrium conditions over the entire operational range. Once the entire thermodynamic conditions with enriched water are determined, they will be contrasted with the thermodynamic conditions for proton water in order to identify the operation conditions to achieve the desired separation. Upon identification of the operation conditions, experiments will be performed with actual waste samples containing low quantities of enriched water to separate the radioactive and nonradioactive components. Samples of the feed and product will be taken and analyzed to determine the separation factors.

In Situ Bioremediation of Non-Aqueous Phase Liquids

Brent M. Peyton and Rodney S. Skeen (Process Technology and Engineered Systems)

Project Description

With the current absence of methods for locating pools of contaminants underground, methods for in situ remediation of these pools of non-aqueous phase liquids (NAPLs) must be explored. One such promising remediation method is the enhancement of in situ biological activity through nutrients and surfactants. This project developed a unique bioreactor to allow visual observation of biofilm formation at the organic/water interface. Background information was collected to provide a range of microbial tolerance limits to contaminants of interest.

Non-aqueous phase liquid (NAPL) pools form when an insoluble organic liquid contacts the saturated zone of an aquifer. The NAPL then tends to form pools at the top or bottom of the saturated zone. These pools remain in the subsurface as high concentration contaminant sources that because of viscous forces and capillary pressure, are untreatable by common pump and treat technologies. The current method of NAPL remediation relies on locating pooled NAPLs, installing a well, and pumping the liquid to the surface. The problem with this technique is that it is extremely difficult to locate the NAPL pools. One technique that could by-pass the need to locate individual NAPL pools is to enhance in situ biological activity through the subsurface addition of nutrients and surfactants. The goal of this project was to demonstrate in situ biological destruction of NAPLs thereby obviating the need to locate pockets of NAPLs.

Technical Accomplishments

This project used a microbial consortia obtained from Hanford soil cores to determine to what extent the Hanford consortia could be used to degrade subsurface NAPLs. By developing a layer of microorganisms at the NAPL interface, this "biofilm" would slow the transfer of the contaminant to the aquifer in two different ways:

1. Mass Transfer Reduction - The biofilm would act as a mass transfer boundary layer that would retard the diffusion of the contaminant to the aqueous phase. In addition, the diffusion coefficient for mass transfer through biofilms is less than for water alone. The reduction in the diffusion coefficient combined with the increased distance for mass transfer will slow the release of contaminant to the aquifer.
2. NAPL Destruction - The microorganisms would also degrade the contaminants as they diffuse through the biofilm, further reducing the transport of the NAPL into the aquifer.

A flow cell was developed (Figure 1) and used to allow visual observation of biofilm formation at the NAPL/water interface. The flow cell was equipped with vertical ports at the top for application of the NAPL, cyclohexane, to the porous media which had been inoculated with bacteria from the DOE Hanford Site. Cyclohexane concentrations were measured daily and were reduced to below detection limits in a few days. In addition, effluent viable cell concentrations were measured using plate counts and remained stable after 175 hours.

Contrary to the hypothesis of the proposal, no visible biofilm was observed to develop on the NAPL interface. This was a disappointment since one of the project's objectives was to visually observe and photograph a biofilm in porous media in situ and undisturbed. However, indirect measurements of biofilm accumulation were made. These measurements include the continuous production of cells throughout the tests. After stabilizing at 5 x 10^5 CFU/mL, the biomass accumulated in the porous media reactor continued to produce cells at this rate throughout the remaining 200 hours of the tests. Another measurement of biomass accumulation in the reactor is shown in Figure 2. This figure shows the protein concentration with location through the reactor at the end of an experiment. It can be seen in Figure 2 that the highest protein concentrations were found at the top of the reactor where the NAPL was located. Although the project demonstrated that cyclohexane was degraded and biomass did preferentially accumulate in the regions near the NAPL, the accumulation of a biofilm at the NAPL/water interface was not visually observable. Therefore, further funding was not pursued for this project.

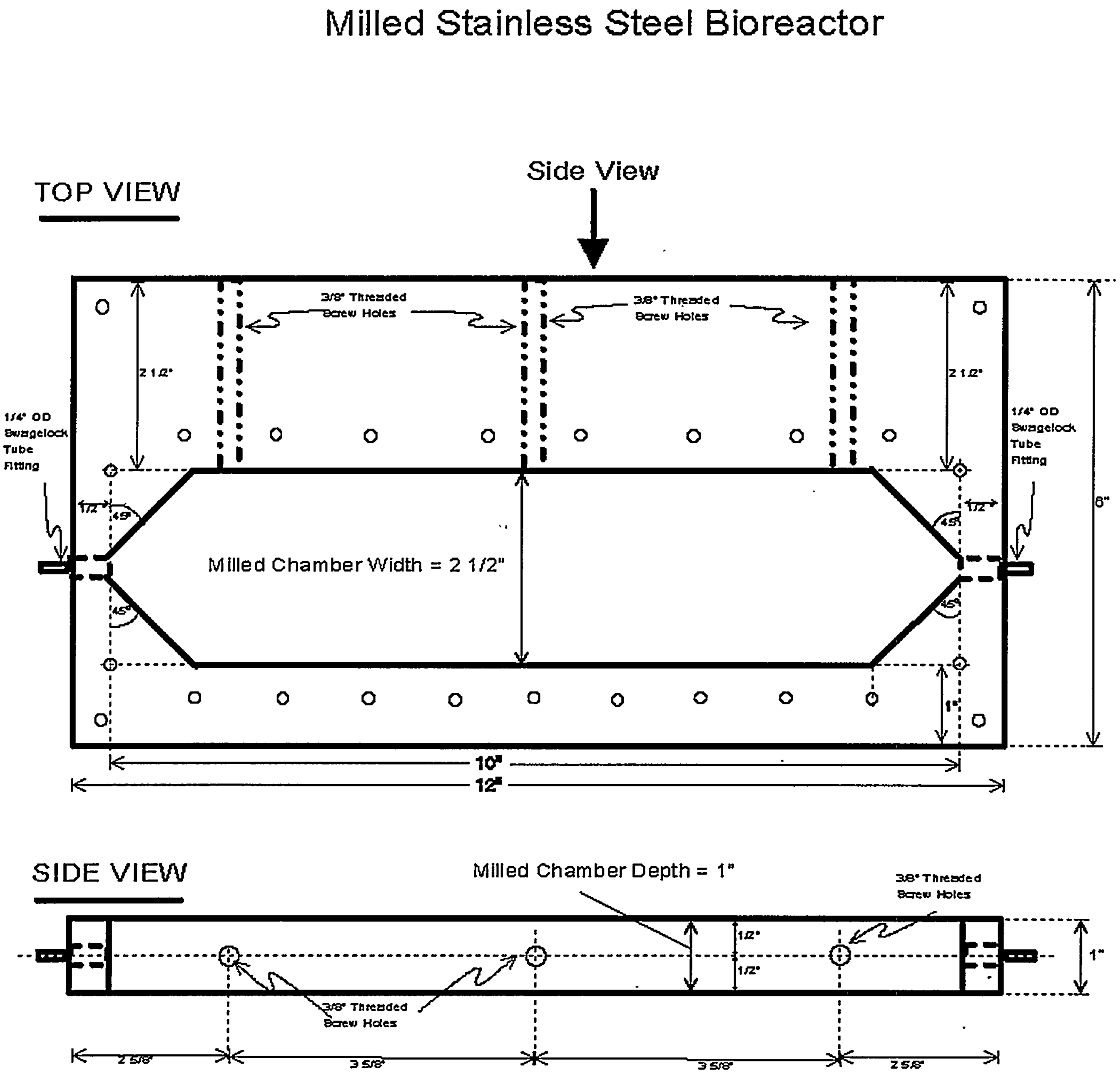


Figure 1. Porous Media Bioreactor with NAPL Ports Used in Experiments

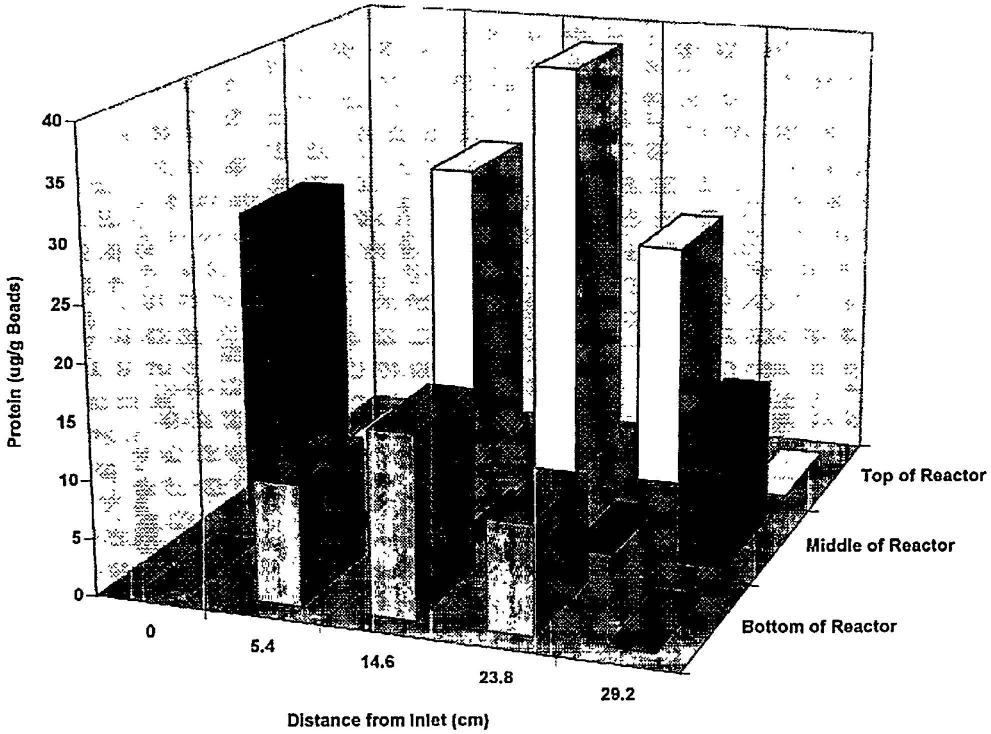


Figure 2. Protein analyses at the end of experiments indicate that the highest biomass density was near the NAPL-water interface.

In Situ Containment Using Heat-Enhanced and Carbonate Barriers

Gautam Pillay, Phillip A. Gauglitz, Rahul R. Shah, and Steven R. Billingsley
(Process Technology and Engineered Systems)

Project Description

The primary objective of this project was to study the ability of electrical soil heating to emplace in situ barriers selectively in a laboratory-scale apparatus using unique classes of materials. The application of the six-phase soil heating (SPSH) process for the emplacement of electrorheological barrier materials was studied. This project also studied the formation of a subsurface carbonate barrier. Emplacement methods for the formation of a carbonate barrier in a laboratory-scale vessel were tested for proof of principle.

A pressing need exists in the DOE community for reliable methods to install subsurface barriers that function as secondary containment to landfills or underground storage tanks. It is also necessary to develop methods for verification of the integrity of barriers that are installed at these waste storage sites. The barrier materials used at these sites must flow readily in soil, possess low permeability once they are solidified, be resistive to radioactivity and potential chemical attack, and be non-toxic. Two novel barrier concepts were studied in this project.

The concept of the heat-enhanced subsurface barrier uses a proven PNL technology known as six-phase soil heating (SPSH) to ensure the distribution of barrier material around a tank. Originally developed for the heating of soil to remove volatile and semivolatile organics from soil, SPSH slowly heats the soil within an array of electrodes to a predetermined, controlled temperature. As the heating process ensues, the soil around each of the cylindrical electrodes inserted into the ground begins to dry. During conventional SPSH operation, water is then metered into the soil at the electrode to ensure that electrical conductivity is maintained and that the heating process is continued. For application as a barrier, instead of introducing water, an electrically conductive material will be added. This material, either a thermoplastic polymer, microemulsion, or electrorheological fluid, will follow the heated area around and beneath the tank, permeating the soil pores. When the electrical heat source is removed, the barrier material is expected to solidify and bond to the outside of the tank forming an impenetrable, structurally sound seal.

The in situ carbonate barrier is formed by reacting solutions of calcium hydroxide with carbon dioxide gas to precipitate relatively insoluble calcium carbonate within the pores of the soil beneath the waste site, thus sealing the pores to form a barrier. This barrier would be similar to natural calcareous formation that are historically impervious to water flow. The expected benefit of this new technology is the assurance of emplacing a contiguous horizontal barrier in situ at a cost that is comparable to conventional slurry wall technology. In addition, the horizontal well(s) that will supply carbon dioxide to form the barrier, provides a means for measuring (or monitoring) the integrity of the barrier after installation.

Technical Accomplishments

Heat-Enhanced Barrier

Scoping experiments were conducted to determine the feasibility of using organic fluids/solids containing electrically conductive particles as barrier materials. Electrical conductivity measurements were conducted on suspensions of fine graphite particles suspended in both mineral oil and a paraffin wax that melted at about 65°C. The fraction of graphite was varied from 0 to 50 wt% in small increments. For both of these nonconductive organic fluids, the graphite particles made conductive suspensions for graphite fractions above 20 wt%.

The next experiment determined the ability of a graphite suspension to flow in a porous soil. A suspension of about 30 wt% graphite in paraffin was injected into a soil column containing glass beads. The paraffin was heated on a hot plate and the column was placed in an oven maintained above 65°C. Experiments with different size glass beads showed that the graphite particles need to be less than 1/20 of the soil particle size for the suspension to propagate through the porous media, which agrees with literature values of the ratio of suspension-particle to pore-throat size. For experiments where the particles propagated through the beads packs, the soil column was cooled and the paraffin slurry solidified. Measurements of the pressure drop and flow of water through the barrier material indicated greater than a 1000-fold reduction in permeability.

Microemulsions of paraffin wax, surfactants, and water are also potential barrier materials. Based on a literature survey, aerosol-O.T (sodium bis-2-ethyl hexyl sulphosuccinate) was selected as a suitable surfactant because of its ability to solubilize large amounts of water in organic solutions and form microemulsions without the addition of a co-surfactant. Sodium dodecyl benzene sulfonate was also selected as a test surfactant, because substantial literature exists on its properties. These surfactants and a series of paraffins were obtained, but scoping experiments were not completed.

Carbonate Barrier

Carbonate barrier formation tests were performed by countercurrently flowing carbon dioxide gas, injected at the bottom of a column filled with glass beads, and a calcium hydroxide solution dripped at the top of the column (at no greater than 100 mL/min). These two compounds under basic conditions ($pH > 12$) formed calcium carbonate. Concentrated carbon dioxide gas (99%) and 0.002 to 0.0025 M dilute calcium hydroxide solution were used for these experiments. Glass beads of 90-micron were used, and the tests were conducted in an unsaturated state. After each test was complete, intrinsic permeability measurements were made using water as the flowing medium.

Several barrier formation tests that investigated different reactant injection techniques were conducted. First, initial barrier formation tests were performed by contacting injected carbon dioxide and dripping calcium hydroxide above the packed bed. By visual observation, calcite formation occurred on top of the bed and very few deposits were observed within the bed.

The second test investigated co-current flow of carbon dioxide and calcium hydroxide. In this test, however, the pH became too low (< 10), and the formed calcite dissolved to bicarbonate and carbonate ions. A clear effluent, instead of the usual cloudy liquid, was collected from the column. Carbon dioxide pressure drop through the bed and final intrinsic permeability were unaffected by these tests.

From these tests, it was observed that calcite formation in the pores of the beads seemed most successful when 99% carbon dioxide was bubbled approximately 1 inch above the bottom of the packed bed at a flow less than 250 mL/min. Calcium conversion from the hydroxide to calcite form was high (approximately 70 to 80%) for all tests. Successful calcite formation tests had $pH > 11$.

Measurements of the intrinsic permeability after the tests indicated no change from the initial permeability.

Barrier Emplacement

Typical barrier emplacement techniques have not been developed with the goal of emplacement of chemical barriers or of flowable barrier material. Most applications involve grout or other cement-based material, or of emplacing lining materials prior to constructing underground containment. However, a literature review found that the techniques that appear to be most applicable to emplacement of chemical or flowable barriers are horizontal drilling and a unique combination of hydraulic fracturing with SPSH.

Horizontal drilling applications have been used in the past by the oil, pipeline installation, and utility installation industries for emplacing horizontal wells in oil fields. This technique may be modified to allow for the emplacement of carbonate barriers. The implementation may take the form of two sets of horizontal wells being drilled, one above the other. The top wells could introduce $Ca(OH)_2$ solution into the soil, and the bottom wells would introduce carbon dioxide (g). The precipitate formed ($CaCO_3$) would form a barrier between the set of wells.

The hydraulic fracturing technique consists of boring a well and using a cutting tool to create 6-inch deep notches into the sides of the well at specific intervals. A mixture of guar gum gel and sand is then pumped into the well, filling the notches and propagating fractures through the media. This results in sand-filled fractures up to 1 inch thick, radiating approximately 30 feet from the bore hole. The SPSH system, with its water-addition system at the electrodes, may potentially be employed in concert with hydraulic fracturing techniques to emplace a flowable barrier. The technique would utilize the same holes for electrode emplacement as well as for flowable barrier material emplacement. After initially boring a well, the electrodes could be emplaced into these wells, and while voltage is applied, a flowable material, such as graphite-doped paraffin wax, can be pumped under pressure into each electrode, utilizing the water-addition system. The electrically conductive graphite in the wax will induce the paraffin wax to flow toward the other electrodes, and the heat from the electrodes would serve to keep the wax in a liquid state. Once the wax has permeated the soil between the electrodes, the power to the electrodes is removed, allowing the wax to solidify in place and form a barrier.

In Situ Monitoring of Ultra-Fine Particle-to-Particle Material Interactions

Jun Liu and Russell H. Jones (Materials Science)

Project Description

This research was directed toward the science of ultra-fine (nanometer) particle and particle-to-particle interactions related to synthesis and consolidation. The solution chemistry and the colloidal properties of fine particles were simultaneously monitored. This kind of particle-particle interaction cannot be adequately described by existing theory, and new consolidation methods needed to be explored. Molecular dynamics computer simulation was also performed for interacting metal particles, which provided information about the diffusion mechanism and the diffusion constant during densification and sintering.

Fine particles have been used to prepare advanced nanocomposite ceramic materials. Three interaction potentials are well-documented: electrostatic repulsion due to charge development on particle surfaces, van der Waals attraction through dipole-dipole interactions, and steric interaction from polymers adsorbed onto the particles. These interaction energies can be estimated using a Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. However, the stability, rheology, and consolidation of fine particles (< 100 nm) has not been well studied. The goal was to understand and model the role of nanometer particle properties and particle-to-particle interactions on consolidation processes. This study included the characteristic properties of these nanometer-size particles, the interactions that occur between the particles, the role these properties have during consolidation processes, and a comparison with consolidation of larger, micrometer particles. The approach included the property characterization of nanometer particles, the determination of particle interaction, and in situ monitoring of the particles during consolidation.

Technical Accomplishments

The solution chemistry of fine alumina suspensions were studied by magnetic resonance, and the aggregation rate and viscosity of the suspensions were monitored at the same time. It has been observed that the hydrolysis process has a large effect on the colloidal properties of fine particles: the increased colloidal stability and reduced viscosity can be directly related to the dissolution and formation of large polynuclear species through aging under acidic conditions. We concluded that these hydrated polycations can significantly modify the total interaction energy between two particles at short separation distances. Figure 1 shows the nuclear magnetic resonance spectrum of alumina suspension aged under acidic conditions. In addition to the broad peak for solid alumina particles and the sharp peak for Al^{3+} ions at 0 ppm, there is a sharp peak at 13.5 ppm corresponding to the polymeric Al_{13} clusters. The hydrated polycations greatly influence the colloidal properties of the suspensions. The interaction energies are also estimated for large separations using the DLVO theory. The conclusions drawn from this study provide a logical explanation for the hydration forces observed in alumina suspensions.

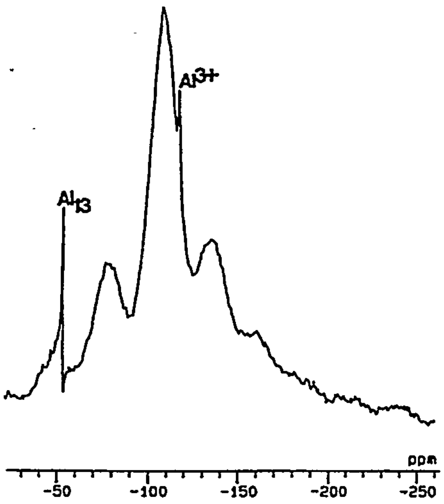
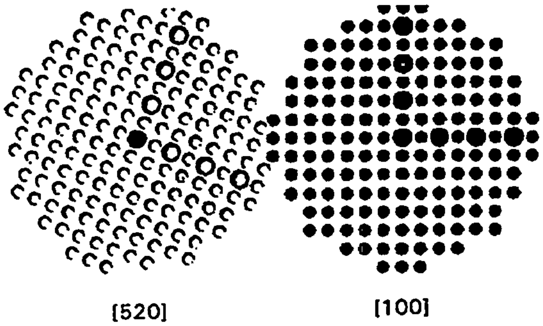


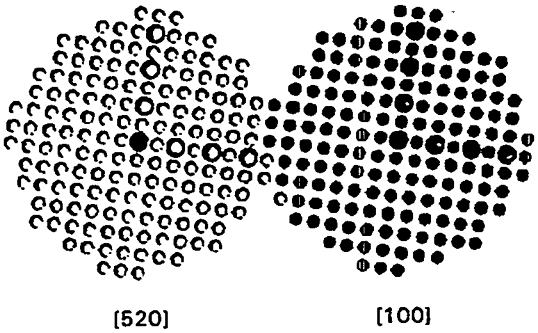
Figure 1. Nuclear magnetic resonance spectrum of an alumina suspension, showing the Al_{13} clusters.

The computer simulation was performed with atomic interactions described by an embedded atom potential for nickel. The interaction and sintering of two particles were simulated. The surface diffusion coefficients were in good agreement with values extrapolated from experiments. The detailed atomic configuration and diffusion process on the surface were also illustrated. Figure 2 illustrates the dynamic process of relaxation and alignment of two particles at T = 0 K.



(a)

INITIAL, T = 0 K



(b)

RELAXED, T = 0 K

Figure 2. Computer simulation during the sintering of two nickel particles.

Publications

H. L. Heinisch. "Computer Simulations of Interacting Metal Nanoparticles." *Nanostructured Materials* (accepted).

J. Liu, J. Virden, B. C. Bunker, and R. H. Jones. "Effect of Hydrolysis on the Colloidal Properties of Fine Alumina Suspensions." *Materials Science and Engineering A* (accepted).

Presentations

J. Liu and R. H. Jones. 1994. "Consolidation of Fine Ceramic Particles." 96th Annual Ceramic Conference, Indianapolis, April.

J. Liu and R. H. Jones. 1994. "The Effect of Hydrolysis on Colloidal Properties of Fine Ceramic Suspensions." Presented at Materials Research Society Fall Meeting, Boston, November.

Investigation of a Treatment Process for Organic Wastes

Michael L. Elliott, Gregory S. Keyes, and Richard A. Merrill (Process Technology and Engineered Systems)

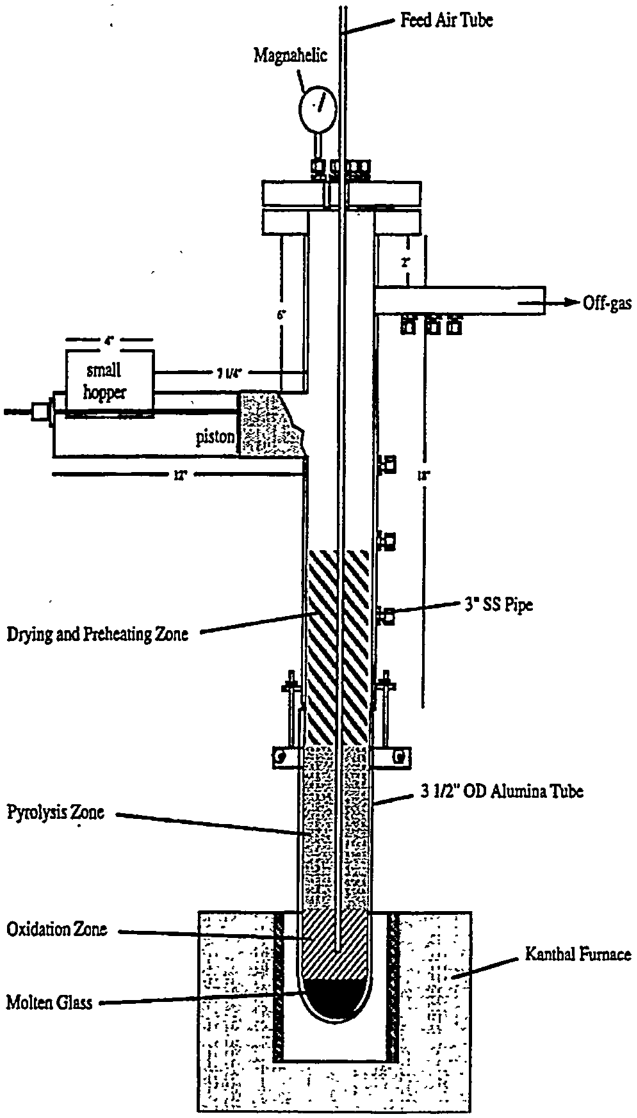
Project Description

An investigation was performed to determine the feasibility of using a single system to thermally treat organic wastes. A prototype bench-scale system that could be potentially valuable for treating low-level wastes, transuranic wastes, sludges, ion exchange resins, bottom ashes, fly ashes, etc., was developed to determine the effectiveness of using one system to both calcine and vitrify organic wastes. This system was used to determine process rate information for various wastes. This information is necessary for refinement of the process and scale-up to a larger system. The bench-scale system will also be an excellent tool to measure oxidation rates as a function of temperature and oxygen concentration for future waste treatment investigations.

Technical Accomplishments

An experimental prototype bench-scale calcination/vitrification system was established in the Engineering Development laboratory of 324 Building. The system consists of a resistance heated electrical furnace, a ceramic crucible, and a stainless steel vertical shaft (see the figure). Feed material is charged to the system through an opening near the top of the vertical shaft. The electric furnace provides the energy to initiate the oxidation and to supplement the energy released during oxidation. Air is injected through a ceramic or stainless steel tube near the surface of the glass melt. The oxygen in the feed is rapidly consumed in the highly exothermic reaction with the charred organic feed. The hot gases move upward, pyrolyzing and heating the feed while cooling the gases. The pyrolysis gases move further upward, preheating the solid feed while being further cooled themselves. The off-gas is then removed from the system. The inorganic fraction of the waste is incorporated into the glass melt.

The system was tested using wood bark as a simple, homogeneous simulant of organic waste material. Glass frit of a known composition was placed in the bottom of the crucible and bark was charged to the system until the crucible and shaft were filled. Power was turned on and the system heated up. It was found that turning the oxidation air on at system startup led to a rapid rise in temperature and fracturing of the crucible due to thermal shock; therefore, the system was heated up to the operating temperature (about 1200°C) prior to initiating the flow of oxidation air into the system. Problems were also encountered with air inleakage at the joint between the ceramic crucible and the stainless steel vertical shaft. Inleakage led to combustion occurring in the upper portion of the feed. This problem was solved by applying a force normal to the sealing surface, thereby reducing the inleakage. The feed was also found to bridge easily, a likely result from the condensation of tars and other heavy hydrocarbons generated during the pyrolysis of the feed material. As a result, the bark in the upper part of the system becomes sticky and is not free flowing. A rod inserted through the top of the system improved the downward flow of the feed.



Test System for Vitrification of Organic Wastes

With the major systematic problems controlled, the system is ready to be used for testing and gathering data. Sustained operations of several hours have been achieved with bark or wood chips. Future tests will expand the range of feed materials and include potential contaminants or simulants of radioactive contaminants to assess the retention of hazardous and radioactive materials in this type of system.

Ionizing Radiation Assisted Processing of Hazardous Wastes

Jiri Janata (Materials and Interfaces)

Project Description

Recent research at PNL has uncovered the possibility of using common photochemical oxidation catalysts, such as TiO_2, as gamma radiation catalysts for the oxidation of organics, or reduction of metal species present in the Hanford tanks. Ionizing radiation (γ,β,α) generates electron-hole pairs in inorganic semiconductors, which should lead to similar surface mediated redox chemistry as that known for optically excited samples. The most common metal oxide substrate for photoelectrochemical reactions is TiO_2, an environmentally benign material. Initial work has focused on studying γ catalyzed chemistry on TiO_2, coated glass beads. Future efforts will extend this study to include wider bandgap oxides, such as zirconium dioxide which is known to be stable in high radiation fields.

Technical Accomplishments

Literature Search

The first activity was a search of the literature using the Dialog interface to Chemical Abstracts. Over 1900 citations were retrieved, complete with index terms. Comprehensive citations covering all of the major relevant chemistry and electrochemistry journals, as well as in-depth coverage of the most relevant topic areas delimited by keyword searching were retrieved. The search strategy employed allowed the minimization of duplicate citation retrievals with 1844 unique citations retrieved out of the total of 1962 citations. This activity resulted in a database of over 1800 papers.

Engineering Bounding Study

Another activity to assess the potential of this process to improve on existing baseline technology was completed. An "engineering bounding" study of a conceptual use of ionizing radiation-assisted processing was initiated. The focus was on a determination of some of the key physical parameters for an irradiator facility for the catalytic destruction of EDTA (ethylenediaminetetraacetic acid) in the presence of a gamma radiation field. Experimental data and theoretical parameters related to this process were used to the extent possible. The system has two primary components: the radiation source and the chemical reactor. Although preliminary proof-of-principle experiments were conducted in a ^{60}Co field, the preferred source material for a number of reasons is ^{137}Cs with a half-life of 30 years and a gamma energy of 01.66 MeV. The ^{137}Cs that is available is stored in the form of cesium chloride salt encapsulated in stainless steel canisters and currently stored in a pool on the Hanford Site with an average capsule activity of approximately 50 kCi. This provides a source strength of greater than 106 R/h at the capsule wall, dropping by about an order of magnitude at a distance of 40 cm.

For the reactor design, concentration of EDTA versus time-of-exposure data was desired but not available due to the nature of the batch measurements made to date. Conservative assumptions were used instead. Conversion rates were calculated for batch, continuously-stirred, and plug flow reactor concepts. The calculation results are summarized as follows:

Reactor Type	Destruction rate, moles/h
1 liter batch	4.1×10^{-4}
1 liter CSTR	5.6×10^{-4}
plug flow	7.8×10^{-4}

The experimental data provided allowed for the calculation of both quantum yield (molecules destroyed/photon) and G-value (molecules destroyed/100 eV of energy absorbed). The G-value is seen as the most relevant parameter for this concept, and was found to range from 4 to 6 in the presence of the catalyst, but was only from 2 to 3 without. The catalyst surface area was calculated (assuming a turnover rate of 1.0 molecule reacted/second/site, and 10^{15} reaction sites/cm^2) to be 0.27 cm^2/gram. This is too small, and suggests that the reaction is much faster.

The ideal reactor configuration for implementation would be the plug flow design, using a series of pipes to carry the solution close to the underwater capsules. The residence time could then be adjusted by changing the flow rate.

Radiocatalysis of EDTA by TiO_2

This activity demonstrated the ability of TiO_2 to catalyze the radiolysis of EDTA. In both ultraviolet and gamma pit experiments, increasing the amount of TiO_2 increased the amount of EDTA consumed. Strontium does not appear to significantly affect the EDTA destruction except when air is bubbled through the solution. Bubbling air through the sample greatly increased the amount of EDTA consumed. The data are summarized in Tables 1 through 3.

Deuterium nuclear magnetic resonance spectroscopy was performed on samples 55585-1a and 55585-1c to help explain the discrepancies in Table 1 between the amounts of EDTA found by ion chromatography and by proton nuclear magnetic resonance. Deuterium incorporation into the methylene position of EDTA was found to be significant in the sample in which gamma exposure occurred in the presence of the TiO_2 catalyst. No deuterium incorporation was found in the ethylene position. This result explains the discrepancy between the nuclear magnetic resonance and the ion chromatography results. The nuclear magnetic resonance shows significantly more EDTA consumed than ion chromatography since there is more deuterium incorporation into the EDTA which is not detectable by proton nuclear magnetic resonance. The ion chromatography analysis gives total amount of EDTA, both deuterated and protonated. This result also shows the point of attack for TiO_2 catalyzed radiolysis is the methylene position between the nitrogen and the carboxylic acid. This and the increased EDTA destruction in the presence of air suggests a free radical pathway as being one possible mechanism for the radiolysis.

Table 1. Gamma Pit EDTA Experiments

Reactions	Run #	% EDTA Consumed		
		NMR Detection	IC(a)	Uv-Vi^sc
No Catalyst(b)	55585-1(c)	0(d)	19	
TiO_2 (0.5 g)(b)	55585-1(e)	48(d)	22	
No Catalyst(b)	54539-141-1	43		
TiO_2 (0.5 g)(b)	54539-141-5	70		
No Catalyst(f)	55585-20-6(c)			2
TiO_2 (3.6 g)(f)	55585-20-6(a)			34
TiO_2 (3.6 g, air)(f)	55585-20-6(e)			71

(a) Ion chromatography using method developed for EDTA detection.

(b) 0.7 mL of 0.0195 M Na2 EDTA exposed to gamma 24 h.

(c) Proton NMR detection based on relative areas of EDTA methylene peak versus capillary filled with chloroform.

(d) The amount of EDTA present is referenced to the no catalyst after gamma result.

(e) UV-visible detection of copper/EDTA complex method.

(f) 5.0 mL of 0.0195 M Na2 EDTA exposed to gamma 24 h.

Table 2. EDTA Destruction by Ultraviolet

Run #	Air?	TiO_2	% EDTA Consumed
55585-1d	No	0	8
55585-73	No	0.86 g	30
55585-7f	Yes	0.86 g	37
55585-1e	No	1.7 g	30
55585-1f	Yes	1.7 g	62
55585-6e	No	3.6 g	60
55585-6f	Yes	3.6 g	81

All runs contained 0.0195 M Na2 EDTA in 5.0 mL of water. Detection of EDTA was by UV-Vis of copper complex.

Table 3. EDTA Destruction in the Presence of Strontium

Run #	Air?	[SR(NO3)3]	%EDTA Consumed By Gamma	%EDTA Consumed By UV
55585-20-3-b,e	No	0.0028 M	18	24
55585-20-3-c,f	Yes	0.0028 M	31	36
55585-20-4-b,e	No	0.0014 M	nd	22
55585-20-4-c,f	Yes	0.0014 M	21	46

All measurements made by UV-Vis detection of copper/EDTA complex. Initial [Na2 EDTA] was 0.0195 M in 5.0 mL of water. TiO_2 1.7 g.

Jet Flows of Complex Fluids

Alireza Shekarriz (Analytic Sciences and Engineering)

Project Description

The objective of this project was to improve the ability to measure, understand, and predict the behavior of jets of complex fluids. The complex fluids being addressed in this project included classes of solid-liquid mixtures, non-Newtonian fluids, and colloidal suspensions; fluids that are often encountered in waste treatment and materials and chemical processing. The basic understanding of how these fluids behave in a processing environment is inadequate, leading to difficulties in process scale-up and inefficient processes. The focus of this project was to perform experimental and theoretical investigations to better understand the effect of particulates and rheology on the flow structure and behavior in process applications.

Technical Accomplishments

Preliminary quantitative flow visualization studies were performed on a submerged pseudoplastic jet. The jet was shown to behave counter-intuitively, in that the traditional Newtonian behavior of a turbulent submerged jet was not observed. These studies further continued during FY 1994 by performing more rigorous experiments using a Laser Doppler Velocimetry (LDV) system. The time-averaged results were consistent with the previous instantaneous velocity maps, in that the yield or strongly pseudoplastic rheology causes the jet to suddenly grow at a much faster rate than a Newtonian jet shortly after it is issued out of the nozzle. These jets seem to exhibit an asymptotic behavior where the jet growth is very similar to a Newtonian jet. This asymptotic behavior was observed at the limit of low apparent viscosity or high nozzle exit velocity.

When the axial distance is normalized by the point of transition of the jet, all the data points collapse on a single curve, which can be represented by a power series relationship. Also the radial distribution of the axial velocity seems to be similar when the radial coordinate is normalized by the radius at which the axial velocity is half of the centerline velocity. These two findings are quite significant, and in fact, suggest that the most important parameters for the design and development engineers are the rate of change of the half-width of the jet and the location at which the jet transition (from inertially to viscous dominated jet) occurs.

Further work on this subject is planned to continue in FY 1995 under the DOE Environmental Management Tank Waste Remediation System program in relation to the double-shell tank mobilization activities. Professor Cill Richards from Washington State University is currently collaborating with the principal investigator on this project, addressing both the issue of submerged viscoplastic jet similitude and turbulence.

Publication

A. Shekarriz, J. R. Phillips, and T. D. Weir. "Quantitative Visualization of a Submerged Pseudoplastic Jet Using Particle Image Velocimetry." *Journal of Fluids Engineering* (accepted).

Presentation

A. Shekarriz, G. Douillard, T. D. Weir, and C. D. Richards. "Rheology and Reynolds Number Effects on the Velocity Field of a Yield-Pseudoplastic Jet." Submitted for presentation at the 1995 ASME FED Summer Meeting, Hilton Head Island, South Carolina.

Materials Evaluation

Robert V. Harris, Richard A. Pappas, and Steven R. Doctor (Automation and Measurement Sciences)

Project Description

The United States infrastructure is in rapid decline because of neglect and lack of understanding of the behavior of materials in the harsh environments they are subjected to. The primitive state of nondestructive material characterization methods prevents timely detection and measurement of the extent of material degradation, which may subsequently lead to catastrophic failure. The intent of this research is to initiate a systematic scientific investigation of the interaction of a variety of probing modalities with the material in order to extract material parameters useful in predicting failure and estimating the remaining life of the structure under test.

Materials evaluation technology is generally oriented toward locating and characterizing flaws. Fracture mechanics calculations are then used to predict crack growth rates, and failure analysis then recommends disposition: repair or increased surveillance. However, often there are no flaws, but failure can still occur because of material property changes induced by radiation embrittlement or fatigue, for example. There are many recent examples of the aging problem appearing in the news and in the Congressional Record. Perhaps the most notorious reports come from the airline industry: some spectacular accidents involving loss of life, blamed on undetected fatigue cracking of the aluminum skin. Other newsworthy reports involve structural failures of highway bridges and predictions of the probable failure of an enormous number of others in the near future. Another important impending problem is the approaching end of the design life of our nuclear power plants, even though there is little evidence of actual danger to the public if their operating life were to be extended. But, there is no way to conclusively prove that the plant could be operated safely for many more years. Thus, there is a need for better sensors and more advanced techniques for nondestructively evaluating the state of the materials used in these massive structures.

Technical Accomplishments

In FY 1993, qualitative observations of acoustic birefringence (shear wave velocity directional dependence) measurements were made, which seemed to indicate a relationship between the magnitude of acoustic birefringence and the sensitization (intergranular carbide precipitation) in 304 stainless steel. The goal during FY 1994 was to verify, and if possible, quantify this relationship. Measurements were made on the same sample set as previously used, consisting of five samples aged 0, 1, 18, 25, and 150 hours. The previous measurements were extended by measuring two to four additional locations on each sample and by measuring the response at increments of 30 degrees of rotation rather than 45 degrees as previously done. The measurements were plotted in polar form to permit a visual assessment of data quality (Figure 1). All measurements were made using piezoelectric shear transducers with shear couplant, with fixtures to maintain the transducer position accurately within 10% of the face diameter and to ensure uniform coupling during the measurements. The result of these measurements was that the variations in magnitude of birefringence between different locations on any given sample were comparable to the variations between samples, which cast doubt on the purported relationship between aging and birefringence.

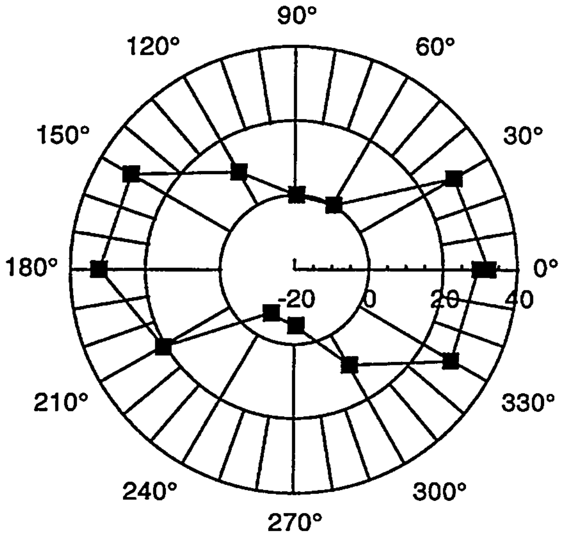


Figure 1. Polar Plot of Shear Velocity

In light of this result, a second experiment was conducted, in which two samples were repeatedly measured, then aged, then remeasured, at successive total aging times of 0, 1, 5, 10, 12, 20, and 60 hours. These observations showed minor fluctuations in the acoustic birefringence, but no clear relationship with aging (Figure 2). The conclusion was that, at best, a weak relationship exists between acoustic birefringence and sensitization.

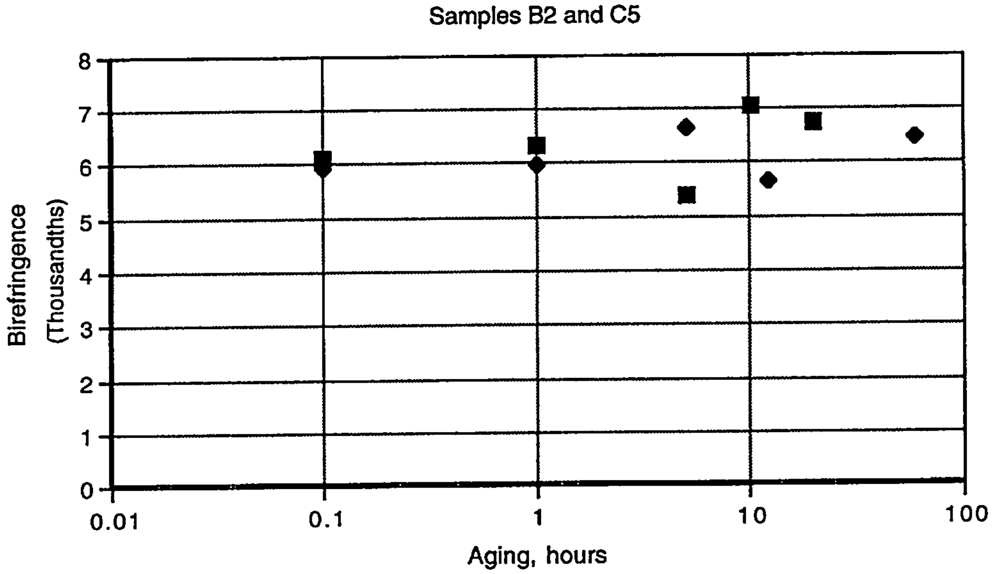


Figure 2. Acoustic Birefingence as a Function of Aging Time

Valuable experience was gained in the technique of measurement of acoustic birefringence using piezoelectric transducers. Polar presentation of the data revealed that one of the transducers had an asymmetric field and was, therefore, unsuitable for use. A surprisingly large positional variation of acoustic birefringence was observed. The use of a high-frequency waveform digitizer (sample interval of 1 to 2 nanoseconds), followed by cross-correlation of the normalized waveforms, allowed accurate and repeatable measurements. These results will be submitted for publication in a measurement technique forum.

Other Accomplishments

Staff participated in a DOE-EPRI-NIST workshop as part of a Research Assistance Task Force (RATF) to address basic science and applied technological issues relevant to life-cycle prediction in structures, and components thereof, as applied in energy-producing utilities and industries.

Membrane Materials

Annalee Y. Tonkovich and John L. Cox (Chemical Technology)

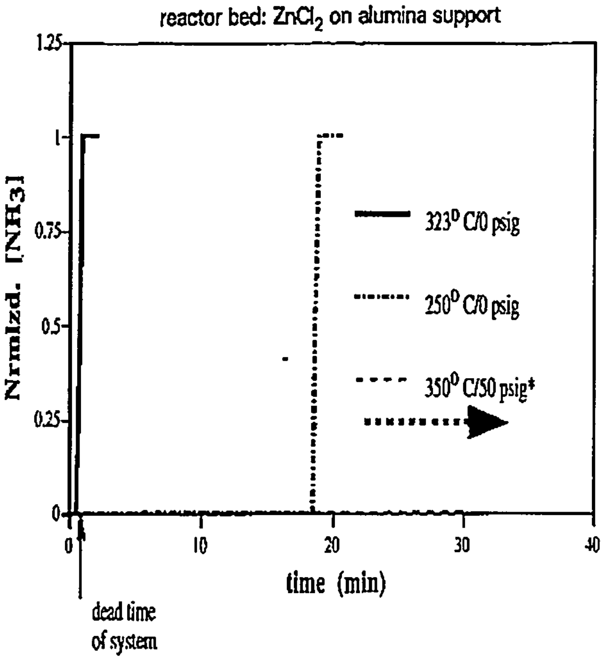
Project Description

The objective of this project was to develop and evaluate new membranes in novel chemical reactors. Thin nickel membranes were evaluated for hydrogen separation in FY 1994, and thin palladium films will be investigated in FY 1995. Novel high temperature sorbents (molten salts impregnated in porous alumina) for eventual use in facilitated transport membranes were also investigated in FY 1994.

Technical Accomplishments

In FY 1994, proof-of-principle experiments were conducted with ammonia sorbing on a molten zinc chloride salt. The zinc chloride was impregnated in porous alumina pellets, and the sorption capacity at elevated temperatures was investigated. Selective ammonia complexation between 250°C and 350°C was observed. However, this material does not readily desorb ammonia and required temperatures up to 500°C at 50 psig to desorb ammonia. The figure presents several ammonia breakthrough curves at elevated temperatures and pressures.

Proof-of-principle experiments were also conducted to evaluate the feasibility of thin Ni membranes for hydrogen permeation. The application of an industrial membrane reactor requires high mass flux rates which near reaction rates. Nickel films of 75 μm were produced and evaluated, but were not thin enough to match fast reaction rates. Membranes which have a thickness reduction of orders of magnitude are required.



Ammonia breakthrough curves for zinc chloride impregnated in porous alumina. Ammonia breakthrough at 350°C and 50 psig occurred after 24 hours. (Breakthrough times less than and greater than dead time correspond to unstable and stable compounds.)

Membrane Separations

Mark F. Buehler (Chemical Technology)

Project Description

In this project, efforts will be concentrated on bench- and pilot-scale membrane research. The results of the project will then be available for application to projected funded development of membrane technologies for the separation and recovery of chemicals from wastes. The results will also be applicable to testing and evaluating new membranes being developed at PNL, such as polyphosphazine membranes. These membranes have the potential to be more robust, suffering less chemical and radiolytic degradation.

Technical Accomplishments

Electro-Membrane Separations

Electrochemical separation techniques are becoming more popular for industrial and hazardous waste applications because of the low operating temperature, minimal secondary waste, and high selectivity controlled by the applied potential. Two membrane-based electrochemical methods were evaluated for their effectiveness to separate aqueous ions from Hanford and industrial waste streams: electrodialysis and electrochemical ion exchange.

Electrodialysis was used to separate both cations and anions using a continuous laboratory-scale flow-cell. Cesium was selectively isolated from a solution with a high sodium concentration using a Nafion 417 cationic membrane. The maximum separation factor for cesium relative to sodium was approximately 3. Spent acid regeneration/separation was also evaluated. Phosphate anions were separated from equal concentration of nitrate ions using an Neosepta AMH anionic membrane. A separation factor of over 10 was obtained and thus, this approach provides an attractive alternative to distillation for spent acid recovery. Finally, low concentration borates were successfully separated from surrogate industrial waste streams using a Neosepta AMH anionic membrane at the limiting current. This application is important for the recovery of borates from chemical processes and power plant cooling water because of new regulations which lower limits for borate discharge. An experimental, laboratory-scale system was assembled for electrochemical ion exchange research. The system included a three compartment flow-cell with the center compartment containing an ion exchange resin sandwiched between two cationic membranes. The system was used to evaluate cesium separation from high concentration sodium streams such as present in the tank wastes at Hanford. Two Nafion 417 membranes were used with CS-100 ion exchange resin. The cesium ion exchange loading and unloading is aided by an applied electric field. This approach successfully reduced the elution volumes needed by 70% when compared to conventional ion exchange separation. Decontamination factors varied from 7 to 10.

Conventional Membrane Separations

Bench-scale capabilities were added to the laboratory in the area of pressure membrane filtration. Systems added include a continuous flow, dual-flat plate stand manufactured by Desalination Systems, Inc., and laboratory-scale batch contactors. Experiments were performed with commercial and PNL-synthesized membranes to evaluate potential applications to water and wastewater treatment. The systems were used to separate and/or recover components from simulated wastes containing inorganic ions and organic chemicals.

Publications

M. F. Buehler, J. D. Norton, and W. E. Lawrence. 1993. *Evaluation of Aqueous Na^+/Cs^+ Separation by Electrodialysis.* PNL-9022, Pacific Northwest Laboratory, Richland, Washington.

J. D. Norton and M. F. Buehler. 1994. "Separation of Monovalent Cations by Electrodialysis." *Separation Science and Technology* 29(12), 1553-1566.

Presentations

M. F. Buehler. 1994. "Electrochemical Separations for Environmental Remediation." Chemical Engineering Department Seminar Series, Washington State University, Pullman, Washington.

M. F. Buehler, P. A. Smith, S. O'Rouke, and M. V. Norton. 1994. "Separation of Ni, Fe, Bi, and Eu from Hanford Waste Streams." Presented at the AIChE National Meeting, Denver, Colorado.

M. F. Buehler, J. E. Surma, and J. W. Virden. 1993. "The Use of Radioactive Tracers in Electrokinetic Soil Remediation." Presented at the National AIChE Meeting, St. Louis, Missouri.

Other Accomplishments

Dr. J. D. Norton, whose work focused on electrodialysis separations, successfully completed a postdoctorate assignment.

Two students affiliated with the Association of Western University were funded to examine the electrochemistry of EDTA and electrodialysis separations of cations and anions.

Mesoporous Materials

Jun Liu (Materials Science)

Project Description

The objective of this research was to explore the synthesis of ordered mesoporous materials and nanoscale structures based on self assembly of ordered structures in surfactant solutions. These materials can be used as ion exchangers for environmental cleanup, catalysts, and catalyst supports.

Many organic systems, such as surfactant solutions, can form a variety of well-ordered structures (liquid crystals) with hexagonal, lamella, and cubic symmetry. If these structures can be used as a template to synthesize ceramic materials, it will generate a new class of materials that can be used in industrial processes based on size and shape selectivity of porous structures, such as catalysis, separation, and chemical sensing. In 1992, ultralarge pore zeolite-like materials were discovered. The new materials are characterized by the pore diameters which can be adjusted between 18 Å and 200 Å through the synthesis conditions, and by the monodispersity and ordering of the pores. It is believed that these molecular sieves are formed on ordered surfactant liquid crystalline structures which act as templates to control and stabilize the ultralarge porous structures.

However, currently only aluminosilicates and a few other materials can be prepared. The objective of this study was to uncover the underlying principles that govern the formation of the mesoporous materials and to develop a methodology that can used to prepare nonsilicate materials that can be used as ion exchangers and catalysts. This project involved characterizing the template structures formed by surfactants; investigating template structure stability, their modification by the inorganic precursor materials, and the interactions between the inorganic and organic phases; growing and stabilizing the inorganic materials within the template structures under hydrothermal conditions; and studying the hydrolysis and condensation of the ceramic precursors during the ordering process.

Technical Accomplishments

We established processing capabilities to prepare mesoporous materials under mild hydrothermal conditions. Aluminosilicate material has been duplicated in our laboratory in a very short time.

We studied the fundamental mechanisms of the formation of mesoporous aluminosilicate and discovered the heterogenous nucleation mechanism. It was shown that colloidal particles promote the formation of these materials. Under similar conditions no ordered structure is observed without these particles. The heterogeneous nucleation mechanism is supported by direct evidence from transmission electron microscopy. Figure 1 shows the ordered materials (indicated by the arrows) grown directly on the edge of colloidal aggregates.

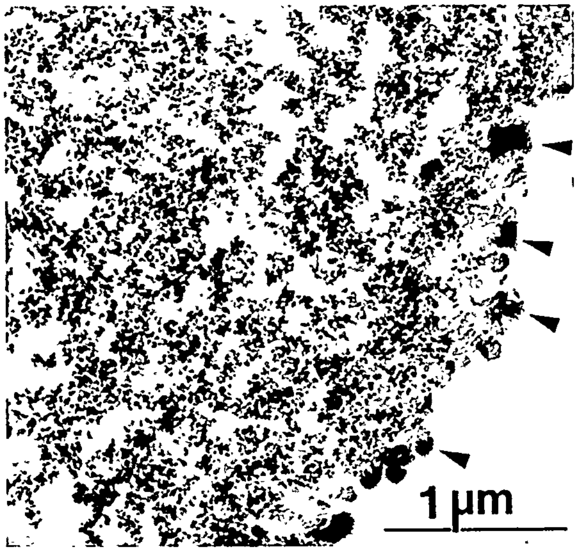


Figure 1. Ordered Materials (indicated by arrows) Grown Directly on the Edge of Colloidal Aggregates

Multicomponent systems are difficult to prepare because of the difference in the reaction rates of the ceramic precursors with the surfactant and the solvent. A nonaqueous route was designed to promote homogeneous mixing of the ceramic precursors and to control the hydrolysis rate of the most sensitive component. A silicotitanate material (Figure 2) was prepared this way with the highest Ti concentration reported so far in mesoporous materials.

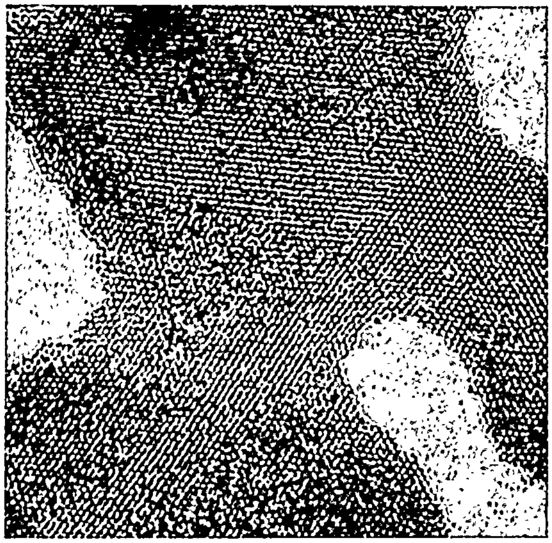


Figure 2. Silicotitanate Material Prepared with the Highest Ti Concentration in Mesoporous Materials

Publication

J. Liu, A. Y. Kim, J. W. Virden, and B. C. Bunker. 1994. "Effect of Colloidal Particles on the Formation of Mesoporous Materials." *Langmuir* (submitted).

Presentations

J. Liu, A. Y. Kim, J. W. Virden, and B. C. Bunker. 1994. "Heterogeneous Nucleation of Mesoporous Materials." Presented at Materials Research Society Fall Meeting.

A. Y. Kim, J. Liu, J. W. Virden, and B. C. Bunker. 1994. "Nonaqueous Synthesis of Mesoporous Materials." Presented at Materials Research Society Fall Meeting.

Microtechnology Applications in Waste and Chemical Processing

Charles J. Call, Richard A. Brouns, and Robert S. Wegeng (Process Technology and Engineered Systems)

Project Description

The goal of this research was to analyze the application of microtechnology to separations techniques. Particular emphasis was given to nonequilibrium approaches, since several have a performance scaling favorable to scale reduction, and thus offer improved performance on the microscale.

Technical Accomplishments

A review of the literature turned up a large number of publications and government reports on nonequilibrium separation processes. Each was analyzed with respect to potential advantages which result from scale reduction. Relative advantages are determined on the basis of the "separation factor" which is defined in terms of the mole fraction of the desired specie in the enriched product stream relative to the same mole fraction in the waste product stream. Most equilibrium processes have a separation factor which is a function of the thermodynamic properties and the molecular weights of the feed components. Nonequilibrium separation techniques have a separation factor which often depends on transport coefficients as well. In addition, each stage of a nonequilibrium process requires some form of continuous energy input which drives the separation. Thus, nonequilibrium processes are generally energy intensive and have lower thermodynamic efficiency.

The gas centrifuge uses gravitational or centrifugal fields to separate gases of different molecular weights. In effect, a pressure gradient produces a concentration gradient. The rate at which the gradient is established depends upon the mass diffusivities of the species as well as the pressure gradient. For those devices which create the gradients via angular rotation, the rate of transport is proportional to the square of the frequency and the first power of the radius. The separation is an exponential function of the square of the product of the frequency and radius. Thus, large structures are better than small ones, but current research on microscale centrifuges indicates that frequencies above 106 Hz are attainable. As a consequence, microscale centrifuges do hold some potential as gas separation devices.

Thermal diffusion separation relies upon a temperature gradient to establish a concentration gradient. This effect is captured by the exact kinetic theory of gases. In real gases, the lower molecular weight specie of a mixture concentrates at the higher temperature zone within the temperature field. The separation factor is proportional to a power of the ratio of the high to low temperatures which are employed to establish the gradient. The magnitude of the separation is usually relatively small. Consequently, thermal diffusion tends to be inefficient since energy is continuously consumed to support the temperature gradient. The energy efficiency on a unit mass basis is not affected by scale reduction.

Other nonequilibrium separation techniques include gaseous diffusion and mass sweep diffusion. The scaling of these techniques is invariant for optimum performance (i.e., the scale of the equipment is dictated by process optimization). Thus, they are not suited for scale reduction. The separation jet achieves its separation primary as a result of the pressure gradient induced diffusion which is a consequence of the aerodynamic gradient between the high speed jet and the ambient. The separation factor is a function of the ratio of the molecular weights of the gases. This approach is not widely used because it is more energy intensive (due to the gas compression required at each stage) than gaseous diffusion.

A more detailed analysis of thermal diffusion was completed. Calculations were made regarding the extent of enrichment of oxygen in air and how much time is required to reach steady-state transport at each stage. The heat sink is assumed to be available at 300K. Tables 1 and 2 indicate the results of these calculations. Table 1 shows the steady-state oxygen concentration after one stage as a function of the heat source temperature. Table 2 shows the time-scale reduction which results from decreasing the separation distance between the heat source and sink.

Table 1. Steady-State Enrichment as a Function of Hot Temperature

mole fraction O_2	T_{hot}
0.2102	330K
0.2104	360K
0.2108	450K
0.2114	600K

Table 2. Time Scale to Reach Steady-State as a Function of the Separation Between Hot and Cold Reservoirs

L	Time
1 cm	2 hours
1 mm	1 minute
100 μm	0.75 seconds
10 μm	7.5ms

Although some advantages to scale reduction are observed for nonequilibrium separation processes, the potential gains do not appear of offset the inherently low efficiency of such separation techniques. Future work will focus on scale reduction for equilibrium processes. The potential advantages include small size, improved process control, and reduced manufacturing costs.

Nanoparticle Materials Development

Charles H. Henager, Jr. and Russell H. Jones (Materials Science)

Project Description

This research was directed toward the science of composite materials using nanometer-scale powders in solid-state displacement reactions.

Reactions where two or more elements/compounds undergo reactive phase transformation to yield new product compounds are referred to as displacement reactions. The ability to fabricate in situ composites with unique microstructural features coupled with improved mechanical properties makes displacement reactions a unique processing route.

This project is related to and is building on the project entitled, "In Situ Monitoring of Ultra-Fine Particle-to-Particle Interactions," (a portion of the project used aqueous synthesis methods). Recent work on displacement reactions have been the synthesis of $MoSi_2$/SiC from Mo_2C and Si powders. These composites exhibited aligned second-phase reinforcements in $MoSi_2$/SiC composites. The mechanical properties obtained were better than the same composites processed by other routes. Theories of phase transformations suggest that the microstructure could be refined (made smaller) and the reaction temperatures reduced by using nanoscale starting materials. These would have advantages in producing ceramic joints, for example, or where mechanical properties would benefit from fine-grain sizes.

Technical Accomplishments

Displacement reactions were initiated between Mo_2C and Si using thin, sputter-deposited layered structures and between ZrO_2, Al_2O_3, and SiO_2 powders processed in solution.

Sputtered layers having submicron dimensions were used to reduce the starting reactant sizes and diffusion lengths in the case of the Mo_2C + Si reaction because nanoscale powders of Mo_2C would be difficult to fabricate. However, since much work has been done at PNL on the science of processing nano-scale powders of oxides, a displacement reaction between oxides was also selected for this research. A reaction between $ZrO_2 + SiO_2 + Al_2O_3$ powders in solution was chosen to explore this route.

Although considerable effort was expended, good, uniformly thin cross sections of the reacted material were not obtained. Results were obtained on the material annealed for one hour at 950°C and this is a good representation of an advanced state of the reaction. Scattered thin areas could be analyzed so that a reasonable picture of the overall microstructure was obtained. The transmission electron microscopy results confirm the extent and phase analysis of the displacement reaction deduced from the SEM analysis. Three regions could be identified: the $MoSi_2$+SiC composite structure, the ternary Mo_5Si_3C phase, and unreacted Si. No unreacted Mo_2C was found. Selected area diffraction revealed primarily regions of $MoSi_2$+SiC separated by the ternary phase. A closer examination of the $MoSi_2$+SiC regions shows columnar $MoSi_2$ grains growing within the ternary phase. Although the ternary phase could be identified through electron diffraction, it was, in general, always thicker than the disilicide phase region and could not be imaged very well.

Positive identification of the SiC phase was made difficult by the myriad of spots observed in the diffraction pattern. Based on the images that could be obtained, small needle like structures were identified as the SiC phase. From previous studies, it was deduced that the SiC nucleated at the silicon-ternary interface, within the ternary phase itself. It was not possible to observe the SiC within the thick ternary phase, however. Although the interface between the disilicide region and ternary phase was irregular on a submicron scale, an interpenetrating microstructure of $MoSi_2$ and SiC did not develop.

Judging from the curvature of the interface between the disilicide and ternary phases, the disilicide is advancing into the ternary phase. Transformation to the ternary phase occurs as the Si diffuses into the Mo_2C and, based on the small, equiaxed grain structure of the ternary phase, there is a high nucleation rate. The $MoSi_2$ phase is nucleated at the Si/ternary interface and growth of these nucleated grains phases is the preferred transformation mode. The reaction of the Mo_2C-Si layers follows the sequence established in earlier work using larger diffusion couples. The limited data generated here for the growth rates of the respective phases showed that the reaction kinetics for the growth of the ternary phase are in the same range as that for the Mo_5Si_3 phase from bulk Mo-Si diffusion couples.

Oxide displacement reactions were studied between $ZrO_2 + SiO_2 + Al_2O_3$ powders and between $ZrO_2 \cdot SiO_2$ (zircon, $ZrSiO_4$) + Al_2O_3 powders (see the table). The reactions produce ZrO_2 plus $3Al_2O_3 \cdot 2SiO_2$ (mullite) after sufficient annealing time. The formation of mullite at 1400°C for reaction 3 is quite significant because it is a low temperature compared to work by others using conventional powders. However, a fine-grained microstructure was not achieved in either case because the mullite phase, which began as an amorphous glassy phase, was large-grained throughout the reacted solid. The ZrO_2 phase was very fine-grained, though.

Conflicting reports on whether or not an amorphous phase forms prior to mullitization were found in the literature. It is claimed that silica and alumina transform independently up to 1200°C, then react to form mullite. Mullite forms by the reaction of alumina and silica without the formation of a precursor, either amorphous or spinel. Others claim that a noncrystalline material forms prior to mullitization, and has the approximate composition, $Al_2O_3 \cdot 12SiO_2$. This latter result would explain what is happening in the system synthesized here. Materials made by reaction 3 showed similar mullitization stages, but the final product did not contain any detectable zircon.

Based on the results of this project, it was concluded that displacement reactions between nanoscale particles result in composite materials having ultrafine microstructures, and that the reactions proceed at reduced temperatures compared to conventional materials processing.

Phase Development of Oxide Displacement Reactions

Reaction	**Temperature (°C)**	**Phases**
$ZrO_2 + SiO_2 + Al_2O_3$	900	t-ZrO_2 + γ-Al_2O_3
"	1200	t-ZrO_2 + γ-Al_2O_3
"	1300	t-ZrO_2 + Mullite + $ZrSiO_4$
"	1400	(t+m)- ZrO_2 + Mullite + $ZrSiO_4$
"	1600	(t+m)- ZrO_2 + Mullite
Zircon + Al_2O_3	1000	$ZrSiO_4$ + Al_2O_3 (SiO_2)
"	1200	$ZrSiO_4$ + δ-Al_2O_3 + ZrO_2 + SiO_2
"	1300	$ZrSiO_4$ + α-Al_2O_3 + ZrO_2 + SiO_2
"	1400	$ZrSiO_4$ + α-Al_2O_3 + ZrO_2 + Mullite
"	1500	Mullite + ZrO_2 + $ZrSiO_4$ (~45 wt%)
"	1600	Mullite + ZrO_2 + $ZrSiO_4$ (<10 wt%)

Nanoparticle Processing

Timothy R. Armstrong, Beth L. Armstrong, and Jud W. Virden
(Materials Sciences, Chemical Technology, Materials Sciences)

Project Description

The objective of this project was to develop methods of processing nanoparticles into useful engineering forms. It was expected that properly processed materials (e.g., membranes, thin films, and pellets) will maintain their useful materials properties, such as high surface area, unique surface chemistry, and controlled porosity.

Materials fabrication processes were developed to form a bulk ceramic shape from starting materials made from the Rapid Thermal Decomposition of precursors in Solution (RTDS) process. Additionally, nanoparticulate materials made by a combustion synthesis process similar to the glycine-nitrate process were evaluated and compared to RTDS-derived powders. It was decided that no hazardous processing aids (organic solvents) would be used to carry out this project and the process developed must be economical and scaleable so that it can be transferred easily to industry.

Technical Accomplishments

Because of the use of the zirconia system in many projects throughout the laboratory including the catalysts initiative and the solid-oxide fuel cell programs, and because it is well documented in the technical literature, it was chosen as the candidate material for this study. Processing and densification of RTDS-derived zirconia powders were directly compared with commercially available powders (TOSOH) and powders prepared by combustion synthesis methods similar to the glycine-nitrate process.

Combustion Synthesized Powders

Both unstabilized and ZrO_2 stabilized with 8 mol% Y_2O_3 were made using a combustion synthesis method using a buffered fuel mixture (urea/carbohydrazide). X-ray diffraction, particle size, and BET surface area analysis were run to characterize the powders and determine which fuel provided the correct phase of ZrO_2. The resulting powder was calcined at varying temperatures and times. Pellets were pressed from the treated powders and sintered at varying temperatures and times. Green and final densities were measured using the Archimedes method and compared to pellets made with commercial grade submicron sized ZrO_2. Linear expansion was measured for verification of sintering trends.

The effects of calcination were evaluated on the powders. In compacts prepared with unstabilized zirconia, the green density increased with calcination temperatures; however, the sintered density decreased at temperature above 1000°C. This is because of the highly agglomerated nature of the nanoscale powder. As the calcination temperature is increased the agglomerates sinter and become hard. Such hard agglomerates will not fracture during compaction and fill the void space in the die. Consequently, green densities decrease with increasing volume fraction of hard agglomerates. Final densities were not measured for the unstabilized ZrO_2 pellets. Sintered samples failed to maintain shape and density. The samples crumbled due to a phase change to monoclinic at 1075°C.

RTDS Synthesized Powders

The processing of the RTDS material was divided into two forming approaches, wet or dry. The dry processing approach evaluated methods to remove the particulates from their solvent and fabrication methods. Wet processing evaluated slip casting and electrophoretic casting as possible fabrication methods. Traditional forming methods were chosen in order to maintain the criteria of an economical forming process. Both approaches were evaluated concurrently.

Since colloidal dispersions are difficult to use in traditional material forming processes, such as pressing, a method was needed to remove the powder from the acidic (unstabilized and yttria stabilized zirconia) or basic (yttria stabilized zirconia), aqueous solutions in a fashion to control agglomeration. Two approaches were evaluated, centrifugation and spray drying. Centrifugation resulted in gels which needed to be dried, crushed, and sized prior to fabrication. The result was hard agglomerates that could not readily be fabricated and sintered to full density.

Slip casting was pursued as an alternative processing method in which the as-processed suspension could be used for fabrication. Initial experiments attempted to cast pellets on plaster molds with the dilute RTDS suspension. These early experiments showed slip casting of the as-processed solution was unsuccessful. The RTDS solutions were too dilute and the high nitrate content of the suspension attacked the plaster mold causing pitting.

A second approach was to slip cast spray dried RTDS powders. All slip cast samples discolored and broke during drying. Due to the low solids content of the suspensions and contamination of the RTDS powders, work was discontinued until new powders could be synthesized. This work was further hampered because a controlled humidity furnace to regulate the drying of these samples to remove large amount of water is necessary when slip casting to ensure crack free samples.

Electrophoretic deposition was evaluated as an alternative fabrication method; however, due to the limitations of this technique in making large bulk components and the need for concentrated powder suspensions, the work was postponed until a concentrated suspension could be prepared.

Conclusions

The work over the past year has clearly indicated that processing of nanoparticles is nontrivial. Further, it was discovered that the limitations of the RTDS solutions were providing even larger problems than would be applicable to commercial submicron powders. Contamination of the solutions, even at a few ppm, discolored the resulting compacts. The high nitrate content in the solution could not be removed in the spray drying process and with the absorbed water resulted in large weight losses upon heat treatment. Additionally, the presence of nitrates make aqueous processing such as slip casting more difficult.

The hydrated surfaces of the powders due to the high surface area created the largest problem for consolidation. If a compact could be fabricated (at low pressures), it would not survive heat treatment where weight loss from water could be as high as 40 to 50%. The resulting pore volume was so large (0.5 Mm), full densification could not be achieved.

This year showed that traditional forming processes need to be reevaluated or new methods developed to compensate for problems found.

Presentation

B. L. Armstrong. 1994. "Issues of Consolidation of Nanoparticulate Materials." Gorham Internet Conference. Monterey, California, November 14.

Nanoparticle Science

Jud W. Virden (Materials Sciences)

Project Description

This project was focused on laboratory experiments to determine the optimal conditions for dispersing a variety of nanometer-sized particles in aqueous-based solutions. These experiments included measurements of particle size and zeta potential to determine the effect of simple salts and organic or inorganic surfactants on particle consolidation and densification.

The goal was to develop an understanding of the short-range structural forces present between nanometer-sized particles in solution as they relate to the ultimate effect on the processing (i.e., dispersion, aggregation, consolidation, densification, and sintering) of nanometer-sized particles. Short-range structural forces result from the adsorption of ions in solution on a nanometer particle interface.

This work is motivated by the promise that an ultrafine grain structure material will exhibit improved sinterability, reduction in flaw sizes, low temperature creep, and superplastic deformation at low temperatures. This promise will not be realized until nanometer particles can be processed such that the unique size and surface properties are not lost during aggregation, consolidation, densification, or sintering. Successful processing relies on developing a fundamental understanding and control of the short-range structural forces and their ultimate effect on the rate of aggregation, lubrication, consolidation, densification, and sintering of a nanometer dispersion.

Technical Accomplishments

A commercial colloidal zirconia, NYACOL Zr 100, with a particle size below 100 nm was used for some initial studies. A number of different electrolytes were added to the zirconia suspensions in order to collapse the electrical double layer. The rheological behavior of the resulting flocculated system was then investigated using viscometric, strain sweep, and oscillatory test methods.

All of the electrolyte-treated suspensions exhibited shear thinning (i.e., their viscosities decrease as the shear rate increases). However, it was also found that flocculation that occurs upon electrolyte addition results in rheological properties that are strongly time dependent. For example, the viscosity at a shear rate of 100/s of the zirconia suspension with 1 M ammonium nitrate added increased by an order of magnitude over 4 days. This was attributed to the formation of a gel-like surface which continues over long time periods.

Preliminary characterizations of simulated Hanford tank wastes (NCAW sludge) were conducted. Particle size and charge are two parameters that can affect a variety of the processing steps that are planned for pretreatment of the Hanford tank wastes prior to vitrification. Such processes that could be affected include filtration, solid/liquid separations, ion exchange, and slurry transport.

The particle size and zeta potential of sludge simulants were characterized at different stages in a sludge washing process. Particle sizes were in the 0.3 to 30 μm range, as expected for the preparation techniques. In general, it was found that all of the samples contained negatively charged particles, as is expected at high pH. However, as washing decreased the electrolyte concentration of the supernatant, the zeta potentials of the particles increased, thereby increasing the stability of the dispersions. After extensive washing, the samples containing electrolytes on the order of 0.001 M had zeta potentials in the -40 to -60 mV range, adequate to ensure stability with respect to aggregation.

Nanoparticle Synthesis

Jud W. Virden (Materials Sciences)
Mark F. Buehler (Chemical Technology)

Project Description

The Rapid Thermal Decomposition of precursors in Solution (RTDS) process is a leading technology in producing large quantities of nanoparticle oxide materials that can be used for processing nanoparticle materials. The production of these particles was investigated under a variety of processing conditions and the final material properties, such as particle size and yield, were optimized with regard to operating parameters.

Technical Accomplishments

The RTDS process uses high temperature and high pressure to continuously produce nanocrystalline particles. For this project, three tube furnaces were added in series to the exit of the existing RTDS unit. These additional furnaces improved the temperature control of the processed solution to ±5°C and allowed the reaction temperature to reach 350°C. This improvement also minimized safety concerns by reducing the reaction tube skin temperature.

The improved RTDS system was used to produce several nanocrystalline powders including zirconia, yttria-stabilized zirconia (4 and 8 mol%), and a nickel-zirconia alloy. The process temperatures and residence times were varied to optimize the yield and particle size distribution. The nanocrystalline powders produced were used to determine the degree of microstructure control upon consolidation and sintering. Also, as a demonstration of its large-scale capability, the RTDS process was used to produce 1 pound of nanocrystalline zirconia for Oak Ridge National Laboratory.

In addition, a bench-scale spray dryer was set up to dry the RTDS suspensions. The dryer is capable of both co-current and counter-current operation. Co-current operation is achieved by using a centrifugal atomizer, and counter-current operation is achieved by using a dual-fluid nozzle atomizer. Yttria-stabilized zirconia powders were dried by processing RTDS suspensions at 350°C and 2 L/min.

Publications

M. F. Buehler, J. G. Darab, D. W. Matson, and J. C. Linehan. 1993. "Bench-Scale Synthesis of Nanoscale Materials." In *NASA Technology 2003 Proceedings*, 1, 285.

J. G. Darab, M. F. Buehler, J. C. Linehan, and D. W. Matson. 1994. "Nano-crystalline Powders and Suspensions generated Using a Flow-Through Hydrothermal Process, Part I: Characterization." In *Materials Research Society Symposium Proceedings*, 346, 499.

J. G. Darab, M. F. Buehler, J. C. Linehan, and D. W. Matson. 1994. "Nano-crystalline Powders and Suspensions generated Using a Flow-Through Hydrothermal Process, Part II: Applications." In *Materials Research Society Symposium Proceedings*, 346, 505.

Presentation

D. W. Matson, M. F. Buehler, M. R. Phelps, and G. G. Neuenschwander. 1994. "High Volume Production of Nanoscale Zirconia." Presented at the 96th Annual American Ceramic Society Meeting, Indianapolis, Indiana.

Non-Newtonian Fluid Dynamics Measurements

Alireza Shekarriz (Analytic Sciences and Engineering)

Project Description

The objective of this research project was to develop an understanding of the behavior and flow of non-Newtonian fluids. These studies encompass simple viscometric and nonviscometric flows. Understanding the main features and differences between viscometric and nonviscometric non-Newtonian flows is fundamental to many of the problems currently encountered when dealing with flow of colloidal suspensions, polymer melts, and waste sludges.

Technical Accomplishments

From some preliminary qualitative flow visualization studies, it was found that the non-Newtonian flow around a sphere at extremely low Reynolds numbers was not symmetric as would be expected in a creeping Newtonian flow around a sphere. This issue raised some concerns regarding the validity of the conventional fluid dynamics approach for the falling ball rheometry data analysis. Falling ball rheometry has been proposed as a means of in situ rheometry for characterization of the fluids within the waste tanks at Hanford.

Several vector maps of the velocity field around the sphere were found for various conditions. From the profile of velocity in the vicinity of the sphere, the ratio of the shear stress and normal stress contribution to the drag force acting on a falling ball was calculated. It was found that this ratio is substantially higher than is commonly present in a Newtonian fluid. The high contribution from the normal stresses and lack of uniformity in the rate of strain field yield low accuracy of the ball rheometry results for rheological characterization of viscoplastic fluids. Also, by detailed characterization of a viscoplastic fluid using an advanced rheometer and side-by-side comparison with the ball rheometer results, several recommendations were made for analysis of the ball rheometer data.

From these studies, a plate rheometer was experimentally found to be much more effective as a passive in situ instrument for characterization of the contents of the waste tanks. Preliminary quantitative studies show that the boundary layer becomes quickly fully developed over the plate when a plate is dropped at a constant rate through a yield-pseudoplastic fluid. This is a unique result for an external flow. As a result, the flow over a plate is not only viscometric (simple shear) but is shown to have a uniform strain rate field over a major portion of the plate. This is a desirable feature for rheometric measurements.

Presentation

A. Shekarriz. 1993. "Creeping Motion of a Sphere in a Yield Pseudoplastic Fluid." Presented at the 46th Annual Meeting of the Division of Fluid Dynamics - APS, Albuquerque, New Mexico, November 21-23.

Novel Electrosynthesis of Organic/Inorganic Electroactive Polymers Based on Co-Polymerization of Organic Molecules with Cyclic Chlorophosphazenes

Mira A. Josowicz (Materials Sciences)

Project Description

The objective of this project was to develop an understanding of the mechanism of the polymerization of organic-inorganic composite materials and to develop synthesis procedures that would lead to a controlled structural architecture of the novel material. Some unique properties of these materials were investigated in the scope of charge-transfer reactions, which may play a fundamental role in a wide range of applications.

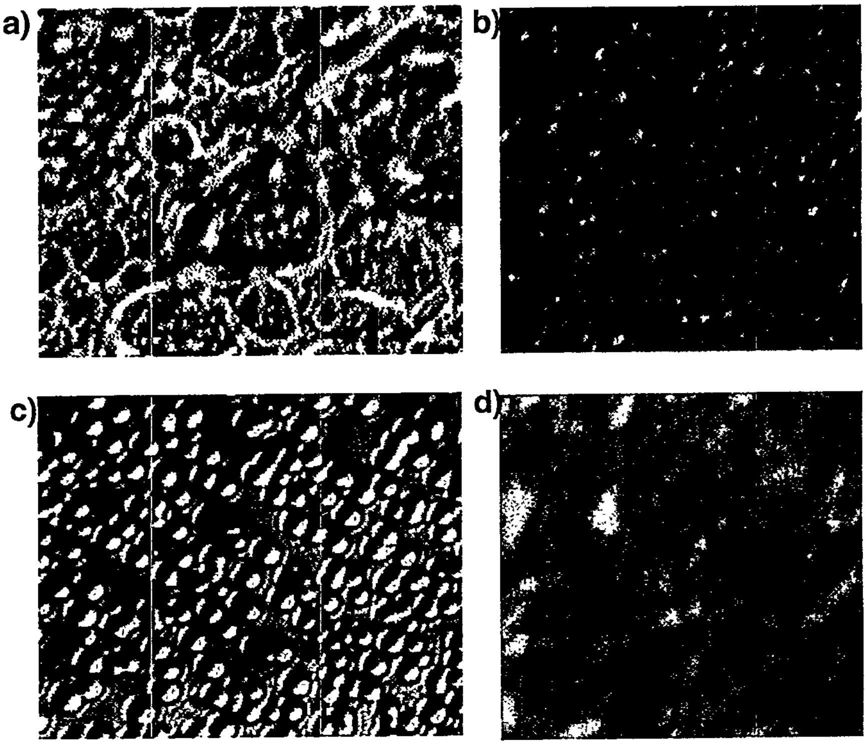
The synthesis and characterization of cyclic polymers of the unique composition of organic and inorganic constituents in the polymer chain is a complex matter. Considerable progress has been made in the molecular-level understanding of the chemical reactivity of the novel materials. Progress resulted from experimental efforts that concentrated on synthesis, optical, spectroscopic, and electrochemical characterization of the novel composite materials.

Technical Accomplishments

In FY 1994, the electrochemical-chemical process for the synthesis of cyclomatrix polymers directly deposited from the hexachlorocyclophos-phazene trimer, $(NPCl_2)_3$, was examined on the following substrates: Pt, Au, Ag, W, Ti, Cu, Ni, Mo, Pb, and ITO. The poly(cyclophophazene-benzoquinone) films, were successfully deposited from the same electrolyte solution under the same conditions on all of the above substrates. This demonstrated that the reductive coupling of an electrochemically generated reactive species from p-benzoquinone to the $(NPCl_2)_3$ through a nucleophilic substitution of chlorine can be significant for future application of novel materials. The polymerization reaction was also carried out in the presence of different organic solvents, such as acetonitrile, tetrahydrofuran, and dimethyl sulfoxide, and it was found that only the first two, in combination with the tested electrolytes, Bu_4NBF_4, Bu_4NI, and Bu_4NBPh_4 could be used. Based on the results of the elemental analysis and x-ray photoelectron spectroscopy of poly(cyclophophazene-benzoquinone) films prepared in acetonitrile containing Bu_4NBPh_4 as the supporting electrolyte (large anion) and Bu_4NI (small anion), it can be stated that no significant incorporation of counter-ion from the background electrolyte into the polymer matrix is taking place.

In addition to these studies, we have investigated the possibility of controlling structural architecture of the cyclomatrix type of inorganic/organic polymers. Central to this effort was to use the same inorganic monomer, the $(NPCl_2)_3$, and to vary the size of the quinone precursor, which actually initiates the polymerization through the electrochemical generation of the quinone radical anion. Anthraquinone (Aq), substituted 1,5-dihydroxyanthraquinone (Antrarufin), and 5,8-dihydroxynaphthoquinone (Nq) were selected as model compounds. Coatings were formed with all the quinone precursors. They differ from each other in morphology, film roughness, and diffraction colors. The figure illustrates the different molecular architectures of the synthesized inorganic/organic polymer films. Furthermore, comparing the optical micrographs of Aq and Antrarufin, the observation can be made that the functionalities placed on the Aq molecule clearly influence the size of the cavities formed between the precursor molecules in the composite material. The formation of different intermolecular transitions by the series of the quinone precursors were also seen in the recorded UV/VIS (ultraviolet/visible) spectra.

Intercalation of iodine into the poly(cyclophophazene-benzoquinone) was carried out by exposing the previously synthesized film to iodine vapor for 2 to 3 days. Due to that exposure, the film changed from colorless to dark brown. Comparison of the UV/VIS spectra of the poly(cyclophophazene-benzoquinone) film before and after iodine doping demonstrates an increased absorption intensity, better resolved absorption bands, and shift of the absorption bands, to higher energy levels. The increase in the absorption intensity of the iodine-doped poly(cyclophophazene-benzoquinone) film suggests an increase of electronic conductivity. Furthermore, when deposited on platinum substrate the novel materials show four electronic transition states at approximately 3.4 eV, 4.1 eV, 4.8 eV, and 5.8 eV. It is speculated that the transition at 4.1 eV and 4.8 eV could be related to the distribution of electrons within the quinone-benzoquinone units connected through the phosphorus atom and the one at 5.8 eV to the π-π interaction corresponding to the



Optical micrographs of potentiostatically synthesized novel inorganic: a) poly(cycloPhz-Bq), b) poly(cycloPhz-Nq), c) poly(cycloPhz-Aq), and d) poly(cycloPhz-Antrarufin) thin polymer films on platinum electrode at constant potential.

width of the bandgap. The lower transition at 3.4 eV may be governed by some electronic states distributed within the inorganic precursor.

The guest species intercalation into the host matrix was investigated by applying an electrochemical process. The iodine doping was carried out in 0.1M H_2SO_4 solution during electrochemical oxidation of 0.01 M KI on the previously modified electrode with the poly(cyclophophazene-benzoquinone) film. During the anodic oxidation of the iodine ion, the potential was swept between 0.2 V and 0.8 V versus the standard calomel electrode with a scan rate of 100 mV/s for 10 minutes. The resulting host matrix was analyzed for its atomic composition before and after the iodine doping. The x-ray photoelectron spectroscopy analysis clearly demonstrated the presence of iodine and a reduction of the chlorine atoms in the composite material. That result demonstrated that an electrochemical substitution of the iodine atom for the chlorine atom in the polymer matrix took place.

In summary, it can be stated that the electrochemically initiated polymerization of hexachlorocyclophosphazene with quinone precursors represents a simple route for synthesis of novel materials with different molecular architecture. The use of substituted quinone precursors during the polymerization process provides easy access for introducing chemical binding sites which can be of interest for nucleation or sorption processes. An additional chemical or electrochemical intercalation of these materials with inorganic species enhances the physical and chemical properties of the materials which mirrors an enhancement of conductivity and provides binding sites for charge-transfer reactions. Recent progress in describing the fundamental properties of novel materials provides the basis for further investigation of the inorganic-organic polymers.

Publication

M. Josowicz, Jing Li, and G. Exarhos. "Novel Electrosynthesis of poly(cycloorganophosphazenes)." *J. Electrochem. Soc.* 141 L162.

Presentation

M. Josowicz, Jing Li, and G. J. Exarhos. 1994. "Electrochemical Synthesis of Poly(Cycloorganophosphazenes)." Presented at the MRS Meeting, Boston, November.

Particle-Induced Turbulence

Lucia M. Liljegren and Clayton Crow (Analytic Sciences and Engineering)

Project Description

Data from this project improved the understanding of turbulence generation through mean slip between fluid and particles in a solid liquid mixture. The data obtained in this experiment complements that obtained in the grid turbulence experiments which focus primarily on the effect of particles on dissipation. The data was used to test turbulence models proposed to describe turbulence generation by particles.

Technical Accomplishments

In collaboration with Washington State University, additional data to improve our understanding of turbulence generation through mean slip between solid and liquid phases was collected. The level of turbulence in the wake region of a settling batch of particles was measured and analyzed. These experiments were performed using index of refraction matched fluids. The path of solid particles was tracked optically using photographic techniques. Measurements have been completed and were reported in Kenning and Crowe (1994). These measurements will be documented further in a Ph.D. thesis by Vannessa Kenning.

Phase Separations

Fadel F. Erian and David M. Pfund (Analytic Sciences and Engineering)

Project Description

The supercritical water oxidation process has great potential for use in the pretreatment of mixed wastes. The solubilities of organic compounds in supercritical water are enhanced, and those of inorganics are reduced relative to ambient water. Thus, the use of this solvent offers the possibility of simultaneously oxidizing organic and separating inorganic wastes. In addition, aggregation of solute and solvent molecules occurs which causes solubilities, and sometimes reaction rates, to be strong functions of pressure as well as temperature. Thus, control of pressure provides an additional way of manipulating the reaction.

In a process which utilizes this chemistry, three conditions need to be fulfilled:

1. Contaminants must be desorbed from the solid matrix into the supercritical solvent.
2. Oxidant and contaminant loaded solvent must be combined.
3. Fine, uniform suspension of solids must be maintained.

The last condition is necessary to allow the development of a continuous, steady-state process which allows no buildup of solids or reaction products. A continuous process is more desirable than a batch process in most cases involving large throughput because of the lower equipment cost and/or higher stream factor of the continuous process. A technology of mixing in supercritical fluid systems needs to be developed to meet these conditions. A cylindrical vessel with several concentric baffles is capable of mixing the fluid and suspending the solids using only the over-and-under motion of the fluid around the baffles without any mechanical mixing. We proposed to investigate mixing in a vessel using a two-dimensional analogue. The flat, multi-pass vessel will represent a vertical section of a cylindrical, baffled vessel. The moving fluid was examined through a series of vertical windows in the face of the vessel. Initial studies will be made using supercritical carbon dioxide instead of water to avoid corrosion problems.

The extent of mixing of contaminant and oxidant streams will be determined using fluorescence spectroscopy. A fluorescent probe molecule will be dissolved in the carbon dioxide—a probe whose fluorescence is quenched by oxygen. A vertical sheet of light from an ultraviolet-enhanced argon ion laser will be used to excite the probe, thus providing a luminous cross section of the fluid. The cross section of the fluid will be viewed at right angle to the laser beam with a CCD-based camera. The second stream containing oxygen will be mixed with the carbon dioxide stream so that the oxygen can react with the probe and quench its fluorescence. Uniform, low fluorescence across the flow path will indicate good mixing between the carbon dioxide and oxygen streams.

Technical Accomplishments

In FY 1994, the requirements for the laser optics and carbon dioxide flow loop systems were determined. A carbon dioxide pump, laser optics, and optical mounts were acquired. Estimates were made of the luminescence from the experiment. From these estimates, specifications for the laser and camera were determined. Several candidate probe species have been selected for batch tests and the necessary chemicals and equipment for such tests were acquired. Flow rates, temperatures, and pressures of oxygen and carbon dioxide were determined and equipment sizing was begun. Preliminary contacts were made with laboratory safety personnel to begin the development of procedures for safe operation of the laser and of the high-pressure oxygen system.

Publications

J. G. Darab, J. L. Fulton, J. C. Linehan, M. Capel, and Y. Ma. 1994. "Characterization of a Water-in-Oil Microemulsion Containing Ammonium Ferric Sulfate Aqueous Phase." *Langmuir* 10, 135.

J. G. Darab, J. L. Fulton, and Y. Ma. "An EXAFS Study of Strontium Ions and Krypton in Supercritical Water." *Journal of Physical Chemistry* (submitted).

T. S. Zemanian, J. C. Linehan, J. L. Fulton, and C. R. Yonker. "Fluid Structure in Supercritical Xenon by Nuclear Magnetic Resonance Spectroscopy and Small Angle X-ray Scattering." *Journal of Physical Chemistry* (accepted).

Presentation

"Interactions Between Reverse Micelles in Supercritical Fluids - Modeling and X-ray Scattering Experiments." Poster presentation at the 1993 Annual meeting of the American Institute of Chemical Engineers.

Other Accomplishments

Performed small-angle x-ray scattering (SAXS) experiments on reverse micelle/supercritical fluid systems at Brookhaven National Laboratory. Also performed extended x-ray absorption fine structure (EXAFS) experiments on ions in supercritical water.

Plasma Engineering and Prototype Development

Theresa M. Bergsman (Process Technology and Engineered Systems)

Project Description

The objective of this project was to perform experimental work to investigate processing parameters for low-temperature plasma processes for liquid and gas treatment. Functional relationships between current, amperage, reactor configuration, and chemical conversion kinetics will be determined. In addition, experimental work will support the development of predictive capability for these processes.

Low-temperature plasma occurs when an electron is accelerated in an electric field until it reaches sufficient energy to ionize gas molecules. Low-temperature, or non-equilibrium, plasma is characterized by high electron energies and low ion or molecular energies. This enables chemical reactions to be initiated at lower temperatures than for conventional technologies. This characteristic may lead to low energy/low cost alternative processes for destroying contaminants in waste streams or producing valuable chemical products. Initial work has focused on destroying organic contaminants in process off gas and waste water.

Technical Accomplishments

In the past year, a low-temperature plasma test apparatus was developed to investigate process parameters for low-temperature plasma treatment of gases. This apparatus was used to determine the electric field characteristics of gas phase reactors to establish scale-up characteristics and support predictive modeling capability of these processes. Electric field properties were measured to assess the relative importance of capacitance and resistance both prior to and subsequent to corona initiation.

In addition, the apparatus was used to investigate various parameters for increasing treatment efficiency and reducing energy consumption and byproduct generation. New catalytic materials showed significant increases in destruction efficiency as well as a decrease in power consumption. Byproducts from the gas reactor were absorbed in water, and liquid phase destruction was also observed indicating a persistence of oxidative species. Increased analytic capability was added to investigate byproduct formation and parameters for NOx formation and destruction. Work was done in collaboration with Lawrence Livermore National Laboratory to investigate the destruction of NOx.

In FY 1994, experimental capabilities were also established to determine overall process kinetics for low-temperature plasma to treat organic contaminants in liquids. Experimental design modifications increased overall destruction rates by greater than five times. A new electrical system was designed so that new electrode configurations could be tested in two new laboratory-scale reactors which can treat between 300 mL and 5 L of solution. This represents an order-of-magnitude increase in the capacity of the laboratory-scale reactor. Between 6 to 8 watts of total power was applied in these reactors.

Data were obtained on the transient current and voltage behavior during tests with several different concentrations of organic dye to judge the effectiveness of the reactor configurations and to optimize the designs of these vessels. This work is applicable to many industrial wastewater problems, such as the treatment of dyes in textile plant effluent streams. Ultraviolet/visible spectrophotometry and total organic carbon analyses were performed on samples of treated solution to assess destruction rates and extent. For example, starting with a methylene blue concentration of 0.006 g/L, the majority of color was removed from the solution in less than 25 minutes. Applied voltage and current were relatively constant throughout the duration of this test, and the average power was 9.55 watts. During these tests, it was also observed that the treated solutions became more acidic during exposure to the corona discharge, possibly due to the formation of small quantities of nitric acid from the discharge byproducts. Also, solution conductivity increased. Work is currently under way using iodometry and an on-line mass spectrometer to quantify and identify the specific reactive species and reaction byproducts of the corona discharge in air, and ion chromatography will help to identify the reaction products in the liquid wastes.

Presentations

W. O. Heath, S. Barlow, T. M. Bergsman, D. E. Lessor, T. Orlando, A. Peurrung, and R. R. Shah. 1994. "Development and Analysis of High-Energy Corona Process for Air Purification." PNL-SA-24432 S. Presented at Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, June 25-30.

G. Pillay, S. C. Goheen, and D. M. Camaioni. 1994. "Development of a Corona Discharge Reactor for Treating Aqueous Organic Contaminants." Presented at the AIChE 1994 Summer National Meeting, Denver, Colorado, August.

Other Accomplishments

J. G. Birmingham was hired at PNL as a Senior Research Engineer in the Engineering Technology Center. Joe has over 10 years experience in developing low-temperature plasmas, holds one patent, and has authored numerous papers in the area.

Reaction Engineering

Annalee Y. Tonkovich and John L. Cox (Chemical Technology)

Project Description

The objective of this project was to develop and deploy a membrane reactor as an energy-efficient industrial chemical reactor. Membrane reactors are a new class of reactors which improve per pass yields for partial oxidation reactions. A porous, but non-permselective, membrane controls the in situ oxygen feed rate to preferentially promote the desired reaction. In industrial practice, a large hydrocarbon to oxygen ratio is used in a traditional tubular reactor design to achieve high product selectivities. Low hydrocarbon conversions per pass result and a large separation and recycle load of the unreacted material is required.

The membrane reactor employs the synergistic combination of simultaneous reaction and separation to improve product yields. The breadth of the work presented in the literature focuses on dehydrogenation reactions using palladium membranes and selective oxidation reactions using dense zirconia or silver membranes. These technologies have not been commercialized in large part because of a lack of suitable materials. Palladium is not cost effective, and the best dense membranes do not permit high mass fluxes for large production operations. In addition, there are no permselective membranes for materials other than hydrogen at elevated temperatures, a feature that would improve the yields of intermediate products.

The approach taken in this effort, in the absence of materials which simultaneously separate ethane and ethylene from methane and oxygen, is to control the reactant compositions during the course of the reaction. A tube and shell reactor configuration is employed, where the hydrocarbon is fed tube-side and the air is fed shell-side. Splitting the air feed along the length of the reactor reduces the local oxygen concentration and thus inhibits the undesired side reactions.

Technical Accomplishments

In FY 1993 a membrane reactor for partial oxidation reactions was designed, constructed, and proof-of-principle experiments were conducted for a simple test reaction (ethane oxidative dehydrogenation). In FY 1994 the membrane reactor was redesigned to improve the performance, and the operating parameters (temperature, feed ratio, and residence time) were characterized experimentally (see Figure 1). Preliminary modeling results were obtained and correlated to experimental trends. The development of a rigorous model to optimize the membrane reactor is under way.

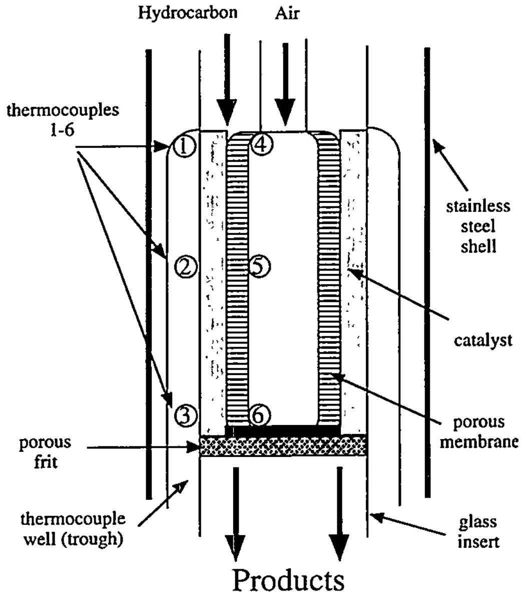


Figure 1. Tube and Shell Membrane Reactor Configuration

The membrane reactors designed and constructed in FY 1993 and FY 1994 have been experimentally compared to a plug flow reactor. The membrane reactor gives higher product yields with low-to-moderate reactant feed ratios and lower yields at high feed ratios. A set of representative yield comparison results are presented in Figure 2. These same trends have been verified with the qualitative mathematical model.

Other novel reactor designs for waste-minimization were evaluated in FY 1994. A collaborative effort was initiated with Professor Fernando Muzzio of Rutgers University to investigate chaotic mixing in stirred tanks.

Poor mixing often occurs in these tanks when viscous reactants and low Reynolds numbers are used, this reduces product selectivities during series-parallel reactions and parallel reactions of different orders. Proof-of-principle experiments were conducted at Rutgers University to demonstrate that chaotic mixing reduces mixing times and thus will improve product selectivity.

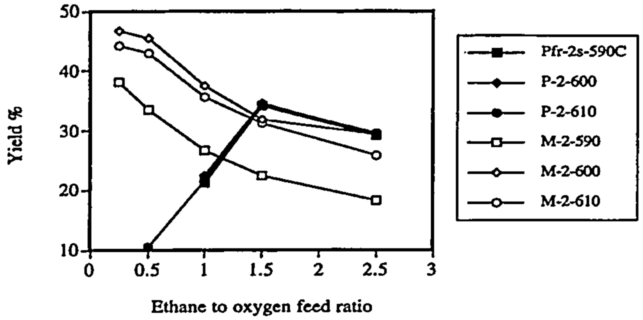


Figure 2. Comparison of Ethylene Yields in a Membrane Reactor (M-) and a Plug Flow Reactor (P-) for a $MgO/Li/Sm_2O_3$ Catalyst

Publications

D. L. Lamberto, F. J. Muzzio, P. D. Swanson, and A.L.Y. Tonkovich. 1994. "Using time-dependent RPM to enhance mixing in stirred vessels." *Chemical Engineering Science* (in press).

A.L.Y. Tonkovich, R. Secker, E. Reed, G. Roberts, and J. Cox. 1994. "Membrane reactor/separator: a design for bimolecular reactant addition." *Separation Science and Technology* (in press).

Presentations

A.L.Y. Tonkovich, R. Secker, E. Reed, G. Roberts, and J. Cox. 1993. "Membrane reactor/separator: a design for bimolecular reactant addition." Presented at the Eighth Annual Symposium of Separation Science for Energy Applications in Gatlinburg.

Experimental results will be presented at the AIChE national conference in San Francisco, California, 1994. Two papers on this work are in preparation.

Invited lectures on the membrane reactor research were presented at Washington State University (November 1993) and Rutgers University (May 1994).

An invited lecture on novel reactor designs, including membrane reactors, was presented at the NIST-sponsored "Research opportunities in pollution prevention for chemists and chemical engineers: an industry perspective" conference in October 1994.

Structure/Function Analysis

Richard T. Hallen and Timothy L. Hubler (Chemical Technology)

Project Description

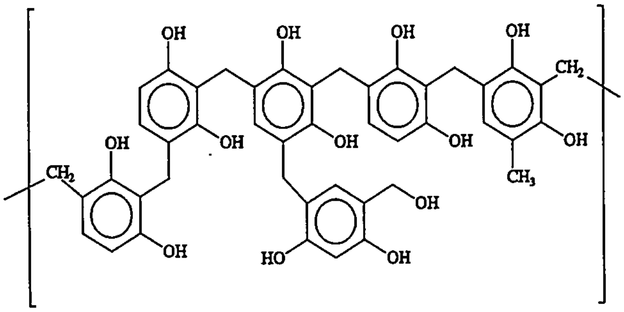
The results of this project will be a fundamental understanding of ion exchange which can lead to improved ion-exchange materials and processes. In this project, the structure/function relationship of phenolic organic ion-exchangers will be determined utilizing spectroscopic techniques such as nuclear magnetic resonance (NMR), Raman, and infrared. Probe molecules and isotopic labeling will be used to investigate the environment of the actual ion-exchange site. Changes in selectivity related to small structural changes or aging reactions will be determined.

Technical Progress

Synthesis of resorcinol-formaldehyde resins was performed according to procedures developed by Wallace and Bibler at Savannah River Technology Center, a variant of the original procedure of Pennington and Williams reported in the literature in 1959. A typical synthesis involves the dissolution of resorcinol in water followed by addition of a KOH solution with stirring. After solution equilibration, formalin was added all at once to the resorcinol/KOH solution with vigorous stirring. The mixture was then cured in a conventional oven at 105°C. The resulting hard glassy resin was ground using a disk mill and sieved to obtain 20 to 50 mesh-sized particles. Synthesizing the resin allowed for the substitution and incorporation of labeled compounds to facilitate structural analysis.

Distribution coefficients (K_ds) for cesium versus sodium were determined using tracer levels of radioactive cesium. The samples prepared at PNL were tested along with resorcinol-formaldehyde resins prepared by Boulder-Scientific and Savannah River Technology Center. The K_d values obtained for PNL synthesized resins were consistently of larger magnitude (more selective for cesium). Preparation of resins under anaerobic conditions to prevent the possible oxidation of the resin had little effect on the value of the cesium K_d. The incorporation of ^{13}C-labeled formaldehyde into the resin had little effect on the K_d, but was useful for structural characterization of the resin. Resins prepared using a standard resorcinol-formaldehyde precursor solution which were cured for 2 weeks at room temperature in an open beaker had very low K_ds. This is most likely due to insufficient crosslinking of the polymer resin as a result of the lower temperature. Curing temperature had the largest effect on resin K_d values. The superior performance of the PNL resin was probably a result of the greater crosslinking due to higher cure temperature and longer cure times.

Solid-state nuclear magnetic resonance and infrared spectroscopy were used to characterize the chemical structure of the resins. These methods showed that the primary unit of the resorcinol-formaldehyde resin polymer is a resorcinol ring with two methylene linkages to form a 1,2,3,4-tetrasubstituted resorcinol ring. Additionally, infrared spectra indicate that as much as 15% of the ring units are 1,2,4,5-tetrasubstituted and/or pentasubstituted. The figure below is a graphical representation of the functional groups and linkages present in the resorcinol-formaldehyde resin. Elemental analysis for the resins prepared at PNL suggests that one molecule of water per ring unit remains after curing, thus most resins are probably composed of at least 10% water (by weight). BET (surface area and pore size analysis) shows that the resins have no internal surface and there are no pores of significant size in the resin. Examination of the ^{13}C nuclear magnetic resonance for some of the resins which had poor Cs^+ ion-exchange properties suggests that oxidation of the resin has taken place to give quinoid structures.



Structure of Resorcinol-Formaldehyde Resin

Presentations

T. L. Hubler and R. T. Hallen. 1994. "Synthesis and Characterization of Ion-Exchange Resins for Selective Removal of Cesium from Hanford Wastes." Presented at the 49th American Chemical Society Northwest Regional Meeting, Anchorage, Alaska, June.

T. L. Hubler and R. T. Hallen. 1994. "Characterization Studies of Resorcinol-Formaldehyde Ion-Exchange Resins for Selective Removal of Cesium in Hanford Tank Wastes." Presented at the 208th American Chemical Society National Meeting, Washington, D.C., August.

Other Accomplishments

Dr. Tim Hubler completed a postdoctoral appointment and was hired as a full-time staff member.

Procedures and techniques were developed which allow the cesium K_d to be determined using nonradioactive materials, thus reducing the volume of radioactive waste generated onsite.

Supercritical Fluids Separations

Clement R. Yonker (Chemical Sciences)

Project Description

Organic chelation of metals has been demonstrated as a method for the selective separation of metals from aqueous streams for such processes as foam separation, solvent extraction, or chelating ion exchange. Recent developments with supercritical fluids indicate that carbon dioxide may prove to be a good solvent for organic chelation agents. This project developed capabilities to study the effects of pressure and temperature on the conformation, chelation equilibria, and kinetics of chelate formation in supercritical carbon dioxide. Operation at pressures and temperatures near the critical point may provide fine control of solubility and enhanced extraction kinetics. The resulting capabilities provided a fundamental background for the development of new separation technologies based upon supercritical fluids.

The sequestration of metal ions and radionuclides is important in the environmental remediation of waste sites throughout the nation and DOE's complex. There are numerous sites contaminated by metals, running the gamut from mining operations and leach sites, to Superfund locations and Hanford. Metal ion contamination in industrial process streams, (i.e., fabric dyeing electroplating solutions and catalysis) amount to hundreds of millions of dollars in lost productivity and remediation costs to industry. Therefore, metal contamination and recovery plays an important role in industrial productivity and competitiveness along with the environmental remediation of hazardous waste sites.

The purpose of this experimental effort is to understand the basic physicochemical behavior of metal complexation in supercritical fluids. With supercritical fluids, density, dielectric constant, viscosity, and mass transport properties can be continuously varied between gas and liquid phase limits by manipulating pressure. The compressibility of a supercritical fluid is large just above its critical conditions, where small changes in pressure result in large changes in the density or solvent strength of the supercritical fluid. As a consequence, molecular interactions can be varied over a considerable range by changes in the intermolecular distance. As the pressure is increased, the solubility of a solute or metal chelate will often increase by many orders of magnitude. These increased intermolecular interactions between the fluid and the metal complex will affect the kinetics and thermodynamics of complex formation and can be used to advantage in extraction schemes once the underlying physicochemical principles are understood. The advantages of supercritical fluids lie in the use of carbon dioxide, which is a cheap, environmentally benign "green" solvent substitute for the typical organic solvents currently in use today in industry. Taking advantage of the dependency of solvent strength on fluid density (which is continuously variable with pressure), and the increased mass transfer rates obtainable using supercritical fluids, one can envision an extraction process in which supercritical carbon dioxide could be recycled by depressurization and recompression.

Technical Accomplishments

In the past year, we have completed the development of a high pressure nuclear magnetic resonance probe. With the novel capabilities of this probe, we have initiated fundamental studies of metal chelation in supercritical fluids. The basic understanding of the structure/activity relationship of the organic ligands in regard to metal ion selectivity and specificity, solubility of the ligand in supercritical carbon dioxide, and ligand recovery from the metal complex obtained from this technique will prove invaluable in bringing this "green" extraction process to reality. These investigations will help guide further refinements in ligand design through the fundamental understanding on a molecular level of the interactions between the metal ion and the ligand and the interaction between the ligand and the carbon dioxide solvent molecule. Studies have been undertaken investigating the solution dynamics of pure supercritical fluid solvents as a function of pressure and density. Initial research efforts have begun involving the investigation of metal complexes in supercritical fluids as a function of density. Ligand displacement reactions using supercritical fluid solvents have been investigated where the fluid solvent has reversibly displaced a complex's organic ligand as a function of pressure and time. This is the first time this behavior has been observed using high-pressure nuclear magnetic resonance. The basic understanding of three areas, ligand solubility, ligand selectivity, and ligand recovery in supercritical fluids is predicated on the fundamental nuclear magnetic resonance spectroscopic investigation of metal complexation under extreme pressure and temperature.

Publications

D. M. Pfund, T. S. Zemanian, J. C. Linehan, J. L. Fulton, and C. R. Yonker. "Fluid Structure in Supercritical Xenon by Nuclear Magnetic Resonance Spectroscopy and Small Angle X-ray Scattering." *J. Phys. Chem.* (in press).

C. R. Yonker T. S. Zemanian, S. L. Wallen, J. C. Linehan, and J. A. Franz. "A New Apparatus for the Convenient Measurement of NMR Spectra in High Pressure Liquids." *J. Magn. Res.* (in press).

Presentations

J. C. Linehan, C. R. Yonker, J. A. Franz, and T. S. Zemanian. 1994. "Scotch Tape, Capillary Tubing, and Superglue: High Pressure NMR." Invited presentation at the Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado.

C. R. Yonker. 1994. "Process Substitution with Supercritical Fluids." Invited presentation at the 2nd National Technology Conference, Charlotte, North Carolina.

Other Accomplishments

C. R. Yonker was named an affiliated Professor of Chemistry at the University of Idaho based on his long standing collaborative ties with Professor Chien M. Wai, Department of Chemistry, University of Idaho. The high-pressure nuclear magnetic resonance probe was nominated for an R&D 100 award by the Laboratory in FY 1994. A multiyear CRADA request was submitted with J. R. Simplot Company as the participating industrial partner and further industrial participation was solicited from British Nuclear Fuels, LTD.

Synthesis of Advanced Coatings

Gordon L. Graff, Bruce C. Bunker, Suresh Baskaran, and Lin Song (Materials Sciences)

Project Description

New coating materials and techniques are important to industry not only to extend the useful life of components but also to allow the substitution of lighter-weight materials and to tailor the surface properties for specific applications. Program research has resulted in new, unique coatings techniques (i.e., biomimetic ceramic layers) and new coating materials such as inorganic polymers. The objective of this project was to demonstrate feasibility of these coatings techniques and materials for various applications.

Technical Accomplishments

The primary focus of FY 1994 research efforts was to improve the deposition conditions (pH, temperature) and deposition kinetics of the solution derived coatings. These factors present major obstacles to the acceptance and widespread use of biomimetic coatings for industrial processes. Typically, the deposition of ceramic oxides from soluble, aqueous salts requires extreme pH conditions ($pH < 3$ or $pH > 10$) to slow the hydrolysis and condensation reactions of the metal ions. To counteract this tendency, the use of metal chelating agents was investigated. Chelating agents, including acetate, citrate, oxalate, and EDTA, were used to complex the metal ions in solution and retard the precipitation of the metal hydroxides and/or oxides. A major success for FY 1994 was a significant improvement in the deposition conditions for SnO_2 thin films. With correct additions of calcium oxalate, the deposition pH was increased from $pH=0$ to 1 to $pH=4$ to 5. Previous film growth at $pH=0$ was essentially prohibitive for industrial applications. Demonstration of film growth at moderate pH was a crucial factor in developing the coatings process for potential industrial clients.

The second factor hampering the potential application of biomimetic coatings is film growth kinetics. During FY 1993, research conclusively demonstrated that the surface modification of polymeric substrates produces a chemically etched volume (typically 1 to 10 microns thick) on the polymer surface. Ceramic film growth then proceeded in two distinct steps on the modified polymer. First, the metal ions rapidly intercalate (minutes) and precipitate within the "etched" polymer region, followed by extremely slow growth (hours to days) of the ceramic film on the outer surface of the substrate.

This growth mechanism made measurement and interpretation of growth kinetics extremely complicated. Therefore, SnO_2 film growth was attempted on model surfaces (Si wafers) in which intercalation was not possible. These studies revealed that SnO_2 growth was on the order of 5 to 10 angstroms per hour. In the case of iron hydroxides, deposition rates were approximately one order of magnitude higher. These rates are still quite slow when compared to plating or vacuum coating methods and must be carefully considered when selecting potential applications of this technology.

Enormous industrial interest was generated during FY 1994 for the solution coatings effort. Over 150 inquiries were made into the biomimetic coatings technique and several led to industrial interactions.

Publications

B. C. Bunker et al. 1994. "Ceramic Thin Film Formation on Functionalized Interfaces Through Biomimetic Processing." *Science* 264:48-55.

B. C. Bunker and G. L. Graff. 1994. "Aqueous Biomimetic Synthesis of Ceramic Thin Films." *Materials Technology*.

Ceramic Industry. October 1994. "Battelle Process Deposits Coatings."

W. Grinthal, G. Ondrey, and G. Parkinson. April 1994. "Surfaces: More Than They Seem." *Chemical Engineering*.

G. L. McVay. 1994. "Miracle Coatings." *Boardroom Reports*.

G. Parkinson. March 1994. "Precipitation Puts Dense Films on Complex Substrates." *Chemical Engineering*.

Ultrafine Nitride Powders by RTDS

Dean W. Matson (Materials Sciences)
John C. Linehan and Beth L. Armstrong (Chemical Technology)

Project Description

The objective of this project was to demonstrate the use of the Rapid Thermal Decomposition of precursors in Solution (RTDS) process as a means of producing ultrafine nitride powders. The RTDS process has been used extensively with aqueous solvents to produce oxide powders. However, its usefulness in nonaqueous systems, which are required to produce nonoxide ceramic materials, had not been fully demonstrated. Nitride powders or their precursors were to have been produced by the RTDS process using high temperature/high pressure liquid ammonia.

Modern high performance ceramics, including Si_3N_4, SiC, and AlN, are manufactured from particulate starting materials that must meet stringent requirements as to purity and grain size. Conventional chemically synthesized powders of these materials typically require mechanical grinding or milling to reduce particle sizes into the micron size range required to achieve the desired microstructure in the sintered bulk products. Mechanical size reduction of these very hard materials is often accompanied by chemical contamination of the powders due to wear of the grinding medium. We have shown that the RTDS process can be used to generate ultrafine powders from metallic salts dissolved in aqueous solvents. Simple oxide products have included a wide range of iron oxide phases, zirconium oxide, nickel oxide, titanium oxide, and zinc oxide. Crystallite sizes in oxide powders generated by the RTDS process have typically been in the 2 to 30 nm size range, with a high degree of crystallite uniformity in any given product run. Particle or aggregate sizes of the powders generated by RTDS have typically been on the order of a micron or less. The RTDS process offers a great deal of potential for producing ultrafine powders of nonoxide ceramic materials, although this will require the use of nonaqueous solvents, including ammonia, which can act both as solvent and reactant under high temperatures and pressures. This project was aimed at developing an RTDS system for use with liquid ammonia and in producing ultrafine nitride powders using this system.

Technical Accomplishments

During FY 1994, an RTDS apparatus was designed and assembled that was suitable for use with a liquid ammonia solvent. Preliminary tests were successfully made confirming the operation of the system using pure ammonia without the addition of a particle forming precursor solute. Work on the project was halted at this point because of the discovery of smearable radioactive contamination in the fume hood where the apparatus was located. Due to the unexpected work stoppage the project was terminated for FY 1994 at that point.

Vacuum Extruded Polymer Films

John D. Affinito (Materials Sciences)

Project Description

The objective of this study was to develop a new vacuum deposition technology capable of depositing polymer, polymer electrolyte, and polymer composite films at a very high rate. A research and development/prototype production vacuum roll coater designed for multilayer thin film deposition onto flexible substrates in a roll-to-roll configuration was adapted for use in this work. The machine is capable of simultaneous deposition of polymer, metal, semiconductor, oxide, nitride, or carbide thin film multilayer structures. This project will develop a process for the in-line, fully vacuum fabrication of electrochromic windows, mirrors, and switches.

The method under investigation involves the vacuum coating of a substrate with a reactive liquid that is subsequently polymerized by exposure to a source of cross-linking radiation (usually ultraviolet or electron). The reactive liquid can be an organic monomer or mixture of monomers, a monomer/salt solution, or a monomer slurred with organic or inorganic particles. These particles could be compound or elemental powders (like oxides, metals, or graphite powders) or high molecular-weight polymer powders.

Technical Accomplishments

To date, we have tested two methods for depositing the liquid layer in a vacuum environment. The PNL web coater employs a slotted die extrusion nozzle to deposit the reactive liquid layer on the substrate. This method was chosen to reduce the total exposed area of liquid in the vacuum in order to reduce the contamination of concurrent processes to as low a level as possible. The flow of reactive liquid into the die head is controlled with a precision metering/degas pump. Using the same metering pump/degas arrangement, an ultrasonic atomizer has also been used to vacuum deposit reactive monomers and monomer/powder slurries.

Figure 1 is a schematic of the vacuum web coater at the Pacific Northwest Laboratory. The chamber is shown configured as it would be for depositing by another process that flash evaporates organic monomers, condenses them, then cross-links them with an electron beam. In the work reported here, an extrusion die head was built and installed in the system to replace the monomer flash evaporators shown in the figure. The die head used the degas/metering pump system that was built for the flash evaporation process.

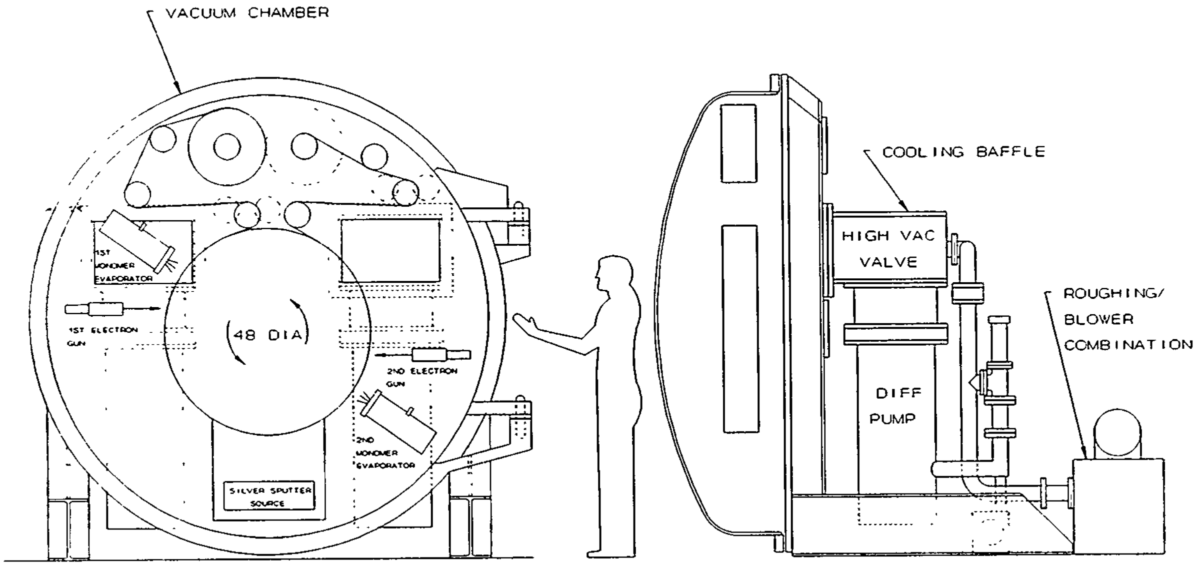


Figure 1. Schematic of PNL Deposition System

A bell jar system was also adapted to spray degassed liquids, and liquid/powder slurries through an ultrasonic atomizer onto rigid substrates then cure the film with ultraviolet light. This system rotated a carousel of nine substrates past the spray nozzle and the ultraviolet source to build thick coatings from many thin layers. This system also used the degas/metering pump system developed for the flash evaporation process.

Vacuum atomized, ultraviolet cured, monomer/CaF_2 slurries were successfully deposited in multilayer stacks of more than 100 layers in excess of 0.5 cm total thickness. Using a single monomer (no index match attempted) it was found that slurry flow, dispense, and cure conditions could be obtained in which, for 0.5 cm thick multilayers, one could not detect crystal dispersion inhomogeneity in the composite with the naked eye. Due to vapor pressure differences between the fluorinated and nonfluorinated monomers, it was extremely difficult to degas the index matched slurry and obtain consistent results in the index of the final material.

Figure 2 shows two samples of polymer/CaF_2 composites. One sample has a very good index match while the other is made from a single, nonfluorinated, monomer. The indexed matched sample has a refractive index of approximately 1.43. Thus it has low front surface reflection. Similar composites, with fluorescing crystals may make very good material for a heads-up display. Since they are very clear, and reflect little, one could see through them without a lot of reflective interference. However, if they were written on with a diode laser, they could be made to emit light to display information.

The vacuum extrusion form of the process was carried out in a roll-to-roll configuration. While thickness uniformity was very poor (due to poor die head/substrate alignment and the homemade nature of the die head) this first attempt did show that the process can be carried out in vacuum under conditions compatible with simultaneous, in-line deposition by conventional deposition techniques.

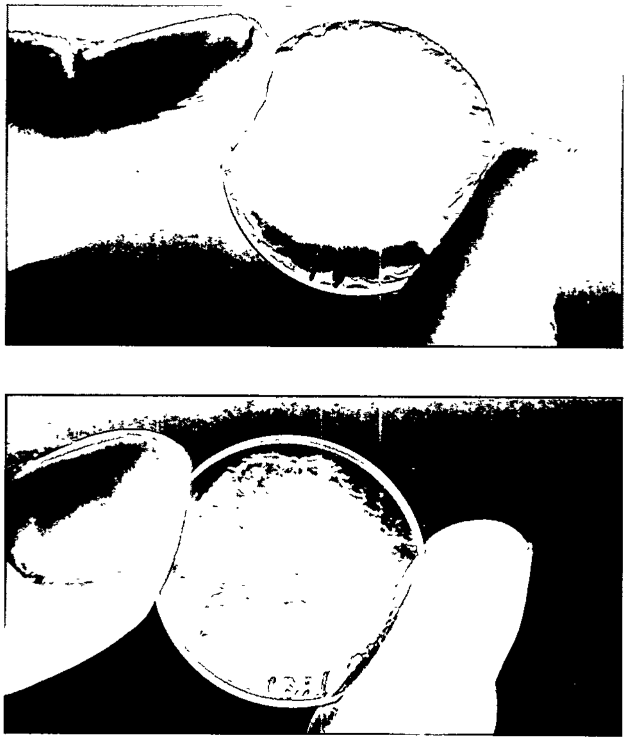


Figure 2. Comparison of two samples, each 10 wt% CaF_2, where the one on the top is index matched by blending fluorinated and nonfluorinated monomers while the one on the bottom employs only nonfluorinated monomer.

The process technology for the deposition and curing of reactive liquids has been demonstrated. The extrusion die/web coating technology will shortly be implemented in programmatically funded efforts to develop processing methods for lithium polymer batteries. The next phase of this LDRD project will develop the die head/web coating process for fabrication of electrochromic devices. The spray, or die head, process should be applicable to deposition of index matched polymer/crystal composites on a plastic web substrate. This could permit low cost, wide area, fabrication of transparent, low reflectance, heads-up display media.

3.0 Energy Systems Development

Advanced Numerics and Visualization for Power Systems

Jeffery E. Dagle (Analytic Sciences and Engineering)

Project Description

Applying PNL's scientific visualization expertise to power systems has been demonstrated for a variety of applications. Visualization can increase comprehension and insight of complex and intricate processes, which is valuable for conveying information in operational, planning, or public relation arenas. Recent breakthroughs in scientific visualization technology, including both hardware and software, have led to imaginative and effective ways of conveying information for a variety of applications, leading to better ways of envisioning information.

The primary project goals were to develop and demonstrate visualization applications for enhancing power system analysis tools. The objective is to improve effectiveness of these tools through better data interpretation using advanced scientific visualization techniques.

The major advantage of visualization is that it directly engages the powerful pattern recognition capabilities of the human eye-brain system. An effective visual representation helps humans generate immediate insights from data, replacing a large part of the processing with computers. Visualization also permits the presentation of much more data to the user. Utilizing human pattern recognition skills, and by communicating the global organization of the results, as well as the results themselves, visualization permits a rapid grasp of the results and their meaning. Natural encoding of the information is important, as it represents data that ties into an existing mental pattern common to most users, and produces a meaning which is intuitively apparent.

There has been extensive work in recent years on developing techniques for power system visualization. These developments are being utilized by EMS vendors to increase the functionality of their product, and have been similarly incorporated into workstation-based engineering analysis tools. Pacific Northwest Laboratory has expertise in scientific visualization technology, developed for a variety of applications. The purpose of this project is to extend visualization techniques to power system applications, utilizing the latest hardware and software available. These demonstrations complement advances in visualization techniques which are being developed by EMS vendors for use in operational environments.

Technical Accomplishments

The first-year deliverables included evaluation of various software packages appropriate for power system visualization applications. Several visualization tools were acquired and evaluated. Using temporary software evaluation licenses, application suitability was determined based on criteria which included product performance, cost-effectiveness (both development and run-time licenses), functionality, and portability.

A proof-of-concept demonstration was developed and a video produced. Perturbations to a reduced-order power system model were simulated using the Extended Transient-Midterm Stability Package, developed by the Electric Power Research Institute. These time-domain simulation results were displayed using DATAVIEWS, developed by V.I. Corporation, with key parameters represented as moving shapes, dials, and colors on the screen. For example, generator speed deviation was displayed with a dial, generator angle as a rotating line, and line current as color. Thus, the equivalent of several time-domain plots can be displayed simultaneously, and presented in an intuitive manner which ensures proper interpretation. In addition to displaying large quantities of information rapidly, visualization also enables the user to quickly grasp the overall situation and readily perceive data relationships much more effectively than by the conventional method of analyzing time-domain plots.

Publication

J. E. Dagle, K. J. Adams, and R. A. May. 1993. "Power System Dynamics Visualization," Video, PNL-SA-23406 A, Pacific Northwest Laboratory, Richland, Washington.

Presentation

J. E. Dagle. 1993. "Power System Dynamic Visualization." Presented at the Visualization Methods for Electric Power Industry Applications Workshop, EPRI, Palo Alto, California, October.

Advanced Power System Dynamic Stability Assessment

Matthew K. Donnelly (Analytic Sciences and Engineering)

Project Description

The scope of this project included the development of an enhanced understanding of the distributed utility concept as it applies to the future power system, an assessment of the analytical tools and models that will be required to study the distributed utility, and a set of studies indicating how the distributed utility will impact certain aspects of future power system operation.

The electric power system is being stressed by delamination, increased competition, and societal pressure to pursue paths that are more economically and environmentally acceptable. At present, utility investment in transmission and distribution is over twice the investment in new generation. Emerging small modular technologies, such as photovoltaics, small gas-fired generation, and energy storage are becoming economic options, when considered as an alternative to transmission and distribution system upgrades. Also, there is significant pressure to increase the utilization of the existing system as opposed to building or upgrading transmission capacity. DOE initiated a program in Real-Time Power System Control and High Capacity Transmission to address these problems.

The topics addressed under this LDRD effort are key elements in a technologic response to the challenges described above. The distributed utility incorporates the idea that generation, using modular and renewable technologies, modular storage facilities, and specially designed customer efficiency programs can be distributed throughout the transmission and distribution system and serve as an alternative to planned central generation investment and transmission and distribution expansion.

The assessment of the dynamic stability of a modern, complex power system requires use of complex simulation and analysis computer models. With the emergence of the distributed utility, the system becomes more complex and many operating decisions will become more challenging.

Technical Accomplishments

In FY 1994, a preliminary assessment of the potential impacts of a distributed utility architecture on electric power bulk transmission system stability was performed. Though there are many other engineering aspects associated with bulk transmission, stability assessment has recently been a prime concern of system planners. There are three recognized types of instabilities within the realm of transmission system dynamics. *Small-signal stability*, or oscillatory stability, deals with very low frequency electro-mechanical oscillations. The physical masses of the system's rotating generators exchange energy with each other through the electrical network. This phenomena is typically associated with very long distance transmission. *Transient instability* occurs when a rotating generator cannot remain in synchronism with the rest of the system in the first few seconds following a disturbance. This is sometimes called first-swing instability and is considered a limiting factor when dealing with medium distance transmission. *Voltage stability* (or instability) is closely related to the system's Var resources. The lack of adequate Var support is usually only a limiting stability factor in a system with closely connected generation and load, i.e., short transmission lines.

Using a reduced-order system and the gas turbine models developed under this project, we produced results that indicate an improvement in transient stability (therefore increased transmission system capacity) under a distributed utility scenario. We are confident that these results will hold for the large base cases we will begin running in early February 1995. In general, we will also see an improvement in small signal stability, but excitation system and protection assumptions will play a large role in those studies. We will continue to develop more valid assumptions so that we can obtain meaningful results.

Presentation

The results obtained under this effort were reported at a Distributed Utility Valuation Project conference sponsored by EPRI, NREL, and PG&E. Similar results were also presented at a panel session of the 1994 IEEE Summer Power Meeting.

Artificial Intelligence for Power System Control

Rex C. Stratton (Information Sciences and Engineering)

Project Description

A number of recent developments have resulted in new challenges to the electric power industry. Among the most influential developments are increased power flow on existing systems, the expansion of distributed automation and demand-side management activities, deregulation, and the installation of generation at the distribution level. Each of these factors creates new constraints on the design, operation, and maintenance requirements of the power system. Advanced automation technologies will play a major role in providing advanced capabilities that satisfy these new requirements and in many cases the focus will be in real-time information development and processing. This project addresses the development of artificial intelligence capability for the power industry. Artificial intelligence technology includes, but is not limited to, neural networks, fuzzy logic, machine learning, and model-based reasoning. The goal of this work was to develop an automated intelligence capability for planning and operations in transmission and distribution activities, develop industry's endorsement and participation in this research, and develop DOE and industry programs that continue this research and development.

Technical Accomplishments

Technical progress included the determination of technical needs and the development of specific technology fundamental for real-time power system control at the distribution level of the power system.

The future of the power industry will depend heavily on its ability to operate more efficiently, reliably, and with higher quality. Management of information is necessary to meet these objectives. Intelligent information technology will move massive amounts of static and real-time system data down the data pipeline and develop information and knowledge necessary for the power industry. Based on these needs, our intelligent information technology development is presently directed toward niche and pervasive technologies. Identified niche technology includes operations planning, real-time distribution control, alarm management, diagnosis, and configuration management. Pervasive technology pertains to system integration and man-machine integration.

In FY 1994 major progress was made on the distribution short-term load forecasting (DSTLF) technology. The DSTLF technology is applicable to both operations planning and real-time distribution control. It consists of four major components: 1) monitored endpoint load forecaster (MELF), 2) non-monitored endpoint load forecaster (NELF), 3) topological integration forecaster, and 4) dynamic self-tuner. These components interact to provide short-term forecasts at various points in the distribution system (feeder, line section, and endpoint). The overall DSTLF architecture and MELF module, for office endpoints, have been developed. MELF is based on artificial neural network technology and predicts distribution endpoint loads an hour, a day, and a week in advance. Predictions are developed using time, calendar, historical, and weather data.

Activities in this project have promoted interaction and collaborations with a number of external institutions. Work with Oakridge National Laboratory has been directed toward developing a program at DOE that focuses on intelligent information technology development. In addition, PG&E has provided guidance in the development of DSTLF. Washington State University is collaborating with PNL to develop a transformer diagnostician and will provide a graduate student to help in this research.

Involvement in professional activities are related to the Distribution Automation/Demand Side Management (DA/DSM) Intelligent Systems Applications to Power (ISAP), and Power Industry Computer Applications (PICA) communities.

Presentations

We will chair several sessions at the 1995 DA/DSM conference, as well as coauthor (with Randy Rhodes of Black and Veatch) a paper that discusses system integration issues.

Asked to be a keynote speaker and chair a technical session at the 1996 ISAP conference.

Also, we are submitting a paper to the 1995 PICA conference, "An Approach to Distribution Short-term Load Forecasting."

Biodegradable Electrostatic Filter Development

Delbert L. Lessor (Analytic Science and Engineering)

Project Description

The objective of this project was to develop a biodegradable form of the Postma-Winegardner electrostatic filter; the application would be fertilizer recovery in a SO_2-NO_x gas cleanup concept. Gas-borne ammonium nitrate and ammonium sulfate particulates can be produced from nitrogen oxide (NO_x) and sulfur dioxide (SO_2) contaminants in a contaminated gas stream, such as flue gas or auto tunnel gas, by injecting ammonia (NH_3) and catalyzing chemical reaction with electrons. The small sizes of the resulting gas-borne particulates of these materials, which are valuable for fertilizer, makes their collection difficult. The Postma-Winegardner electrostatic filter can collect charged particulates of sizes down to tenths of a micron. The Postma-Winegardner electrostatic filter features charging of the particulates in a gas stream by an electrical corona before the flow enters an electrically resistive filter pad, where the buildup of a bed-scale electric field enhances collection. Postma-Winegardner filters have, to date, only used polymer filter materials. If a biodegradable Postma-Winegardner filter of acceptable performance can be developed for this application, the used nitrogen-laden filter can be applied to enhance soil fertility and structure directly, with minimal further processing. Deployment of such a system for flue gas cleanup in coal-fired power plants would produce a byproduct valued at $200/ton instead of $5/ton for gypsum or a negative value because of disposal requirements for the product of some other cleanup systems.

Technical Accomplishments

In experimental investigations in the PNL Aerosol Wind Tunnel Test Facility, we simulated the ammonium sulfate aerosol product of the SO_2-NH_3 reactions by colliding jets of air with larger entrained ammonium sulfate particles, thereby achieving a grinding, followed by injection into a higher flow rate air stream. A corona discharge produced charging of the entrained particles before the flow entered the filter pad. We measured aerosol content of the gas stream upstream and downstream from filters made of candidate biodegradable materials, using both absolute filters and an optical opacity measurement.

We have obtained filtration enhancement from particle charging with both wheat straw and dried grass hay used as the filter medium. Further work is needed to optimize the effect and determine whether the filtration enhancement is coming from simple image force attraction or from the bed-scale electric field buildup which is the key feature in the Postma-Winegardner filter. The bed-scale field buildup lends itself better to higher filtration efficiencies and to application in NO_x-SO_2 cleanup systems. Several other biodegradable materials can also be tried as filter media, such as dried grass clippings, wood fibers (excelsior), sawdust, cotton waste, or animal hair.

An accompanying modeling effort showed that improvement should come from increasing the voltage across the charger electrodes and from increasing the mass loading of the particulates in the air stream.

Cylinder Design for Reduced Emission Origins

Gregory J. Exarhos and Charles F. Windisch Jr. (Materials Sciences)

Project Description

The objective of this project was to develop advanced sensor strategies to probe localized temperature fluctuations and fuel/oil film interfacial chemistry for particular cylinder/piston designs. The foundation will enable designing a combustion chamber for reduced emissions.

To meet stringent new vehicle emission regulations, the U.S. automotive industry must accelerate development of advanced control technologies that reduce engine-out hydrocarbon emissions by minimizing or eliminating their source of generation. The primary hydrocarbon generators in the cylinder are believed to be crevices and cylinder wall oil film storage.

Specific project objectives were to obtain Raman spectra of motor oils and oil films at room temperature and elevated temperatures, investigate ways to improve signal-to-noise and reduce unwanted fluorescence radiation, and set up and test a fiber optic sampling system.

Technical Accomplishments

Before laser Raman studies on the oil film in an actual car engine could be performed, it was first necessary to obtain Raman spectra of motor oils under more ideal conditions. Toward this end, Raman spectra were collected for motor oils in bulk. Over a dozen different types of motor oils were tested. All as-received commercial varieties exhibited severe fluorescence that interfered with the Raman spectra. The water-white basestock of a commercial "Red Line" racing oil showed no fluorescence interference and its Raman spectra was similar to mineral oil. Shifting the excitation to longer wavelengths helped reduce the fluorescence interference for the commercial oils.

Raman spectra were also collected for bulk samples of the basestock of "Red Line" oil as a function of temperature up to 300°C. Significant changes in the C-H stretching region were measured as a function of temperature. Most of these changes were reversible upon cooling as long as the highest temperature reached was about 180°C. At higher temperatures, some irreversible changes were observed. Also at higher temperatures, the oil was observed to "yellow," and result in fluorescence signals similar to that observed for the as-received commercial oils. The Raman spectrum of a 10-micron thick film of the basestock of "Red Line" oil was collected. Bands in the C-H stretch region were observable indicating that spectra of thin oil films were measurable.

Since lower frequency excitation gave better results, a Raman spectrometer was equipped with a new InGaAs detector, which was acquired on loan from Princeton Instruments, and the 1064 nm line of a Nd:YAG laser was used for excitation. This excitation was at the longest wavelength possible in our laboratory and, based on the above results, should have given spectra with the least fluorescence interference. The results were disappointing. Although the fluorescence background was reduced dramatically, the inherently low sensitivity of the InGaAs detector eliminated it from consideration for the engine studies. Based on this study, it was concluded that a Si-based CCD detector was our best option for a detector and that the excitation wavelength should be the longest wavelength compatible with this detector. Pulsed laser/gated detection also appeared to be a requirement to reduce fluorescence and background radiation further and to achieve time resolution of the order of milliseconds.

A fiber optic system, previously purchased from Detection Limit Technology, Inc., Waimanalo, Hawaii, was set up and used with a Spex Minimate spectrometer and diode array detector to obtain the Raman spectra of the basestock of "Red Line" oil. Oil peaks were clearly observable indicating the fiber optic setup should be usable in measuring changes in oil film chemistry.

The above results established important guidelines for future research. In particular, information allowed us to select a laser/spectrometer system that we feel will provide the best chance for obtaining Raman spectra of the oil film in an actual car engine.

Electric Motor/Pump Diagnostician

Richard J. Meador, Francis G. Buck, and Peter J. Galatis (Safety and Performance Analysis)

Project Description

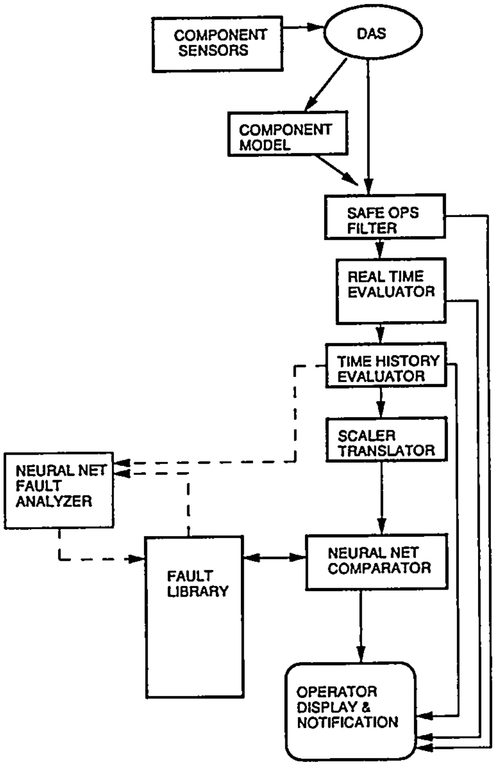
This effort was focused on developing a pump/motor diagnostic methodology that can be coupled to other component models that demonstrate the potential for automated, real-time, integrated degradation and fault diagnosis. The objective of this investment was to complete the proof-of-concept demonstration of the ability to automate the analytical process in diagnosis of selected faults in electric motor/pump equipment.

The objective of this project was to develop a functional real-time diagnostic module for monitoring the operational state and maintenance condition of a pump/driver unit based on some prior concept development initiated in FY 1993. The purpose of this research was to provide the capability for on-line engineering and operational support for reducing both the risks and the cost of operations and maintenance for a centrifugal pump/electric motor unit. Utilizing neural nets and fundamentals of fuzzy logic, this newly developed technology provides a usable computer advisory capability to predict, identify, and diagnose degradation and fault conditions.

Technical Accomplishments

To develop a fully functional on-line diagnostic module or tool for the real-time engineering evaluation of an operating component's condition entails the construction of three main processes labeled the component model, diagnostic evaluator, and fault library. Together, these three segments represent the characterization of the component and its faulted conditions to a level where it can, in a real-time format, monitor, evaluate, and identify the operational condition of the component. The three processes define the mechanism (component) to be evaluated, the condition states to be identified, and how the mechanism (component) is to be evaluated. The above mentioned processes are applicable to any component level mechanism or system (i.e., a pump/driver, a control valve, etc.). When these processes are applied to a component, the main derived portions of the three processes together form the on-line diagnostic function, called the component diagnostic module, or the actual diagnostic tool (see the figure). The remaining parts and information used to develop the tool are retained to provide future enhancement feedback and tool refinements.

The pump/driver unit poses a unique diagnostic situation; two separate functional entities (hydraulic and electro/mechanical) are connected by a common interface—a mechanical coupling device. This set of circumstances allows for an independent simultaneous energy balance to be performed (one from the electro/mechanical side and one from the hydraulic side) using directly measurable information. This comparison provides the diagnostician with the information needed to form a definitive database for the diagnosis of the unit's "condition." Utilizing fundamental principles of fuzzy logic, the diagnostic evaluator then processes this information by reducing it to a stage where a qualitative fault recognition operation can be performed. This qualitative function is performed with the information evaluated in real time (snap shot) and time domain (history) formats. Within the time history format a unique pump performance curve evaluation module was developed to monitor, identify, and diagnose the stressors causing the degradation mechanisms.



Component Diagnostic Module

A qualitative information set from the pump/driver unit is then compared by the use of neural net technology to a reference or library set of "faults" that have been characterized such that each fault is defined by a unique parametric pattern or a unique set of parametric patterns. The fault library serves two functions: it defines the specific parameters needed to diagnose a given fault condition (i.e., what parameters are needed to identify a particular fault) and then provides the logic (parametric) pattern or link between a pre-identified fault and the "actual" condition stream. Additional refinement of the fault logic pattern or characterization is provided by the use of neural networks to aid in the engineering evaluation process. The Neural Net Comparator is provided with collected historical data from the operation of the Component Diagnostic Module and the component to help refine the logic pattern for a fault. Thus, a provision for updating the fault library from operational data is integrated within the process.

The diagnostic module allows on-line engineering support to the operator by displaying "real-time" information on the pump unit's condition. The model also includes automated degradation trending and failure determination, thus providing the information needed to make operations and maintenance decisions with the clear understanding of risks and impacts.

Exhaust System Thermal Management

Mark T. Smith (Materials Sciences)

Project Description

The objective of this project was to develop and demonstrate thermal management concepts for engine support systems to reduce automobile hydrocarbon emissions.

This project focused on demonstration of superplastic forming of stainless steel for doublewall exhaust system components. Double-wall manifolds and downpipes have been shown to conserve thermal energy in the exhaust system during cold-start conditions, resulting in quicker catalytic converter light-off times and reduced hydrocarbon emissions. Superplastic forming technology offers an innovative method for fabricating complex double-wall exhaust systems.

Technical Accomplishments

Results of this project include demonstration of high temperature superplastic forming of stainless steel sheet and basic proof-of-concept of double-wall tube forming. Several sheet pack designs were fabricated and formed during the project, and a low cost, two-piece forming die was developed.

Hydrocarbon Trap Materials

Todd A. Werpy (Chemical Technology)
Suresh Baskaran and Marilou Balmer (Materials Sciences)

Project Description

The objective of this project was to establish a testing protocol (e.g., BET surface area, pore size distribution, adsorption capacity, and adsorption kinetics) for the evaluation of thermally stable inorganic materials for use as hydrocarbon traps. This work was performed on the RXM-100 catalyst testing unit, that was purchased with non-LDRD funds. The classes of materials applicable for this type of investigation include zeolites, pillared clays, and a number of various high surface area metal oxides.

Technical Accomplishments

Expertise in characterizing the adsorption properties of materials has been developed through hands-on training in the use of the new RXM-100 catalyst testing unit. Capabilities developed under this project include surface area analysis, pore size distribution measurements, temperature programmed adsorption studies, temperature programmed desorption studies, and total adsorption capacities for virtually any liquid or gas adsorbate. Continued development of these capabilities has been supported through DOE-EE.

In addition, this project has allowed us to expand our expertise in the area of catalyst characterization and testing. New capabilities in catalyst testing and characterization include continuous on-line monitoring of products via mass spectroscopy, temperature programmed oxidation, temperature programmed reduction, and general gas phase reaction analysis.

Mediation of Combustion Hydrocarbon Emissions

Gregory J. Exarhos (Materials Sciences)

Project Description

Three technological approaches, plasma destruction, photocatalytic oxidation, and metal alloy directed oxidation are proposed as viable methods for removal of unburned hydrocarbon in the exhaust gas stream emanating from an internal combustion engine. Work was directed toward the evaluation of the relative efficiencies of these three approaches toward oxidation of hydrocarbon vapor under conditions which exist in the engine exhaust train.

Reduction of hydrocarbon emission in the exhaust stream of an internal combustion engine immediately following cold start is a significant goal of the automobile industry because an estimated 60% of total engine hydrocarbon emission occurs during this time interval. The catalytic converter, resident in the exhaust train, is effective at oxidizing unburned hydrocarbon only after achieving a temperature of about 800°C. At lower catalyst temperatures, the converter is ineffective and unburned hydrocarbon is released to the air. A system capable of operating between ambient temperature and the equilibrium catalytic converter temperature is required. The time interval for thermal equilibration by the engine exhaust gases is on the order of minutes. It is to this problem and on this timescale that this research was addressed.

Technical Accomplishments

Plasma Destruction

The plasma destruction method (corona discharge), previously developed at PNL and the recipient of several awards, is the most mature technology of the three designated target areas. Emissions destruction was followed in flowing gas reactors and catalytic efficiencies were evaluated as a function of gas composition, flow rate, temperature, and input power to the reactor. Previous work demonstrated that halocarbon destruction occurs readily in a packed glass bead reactor, using glass beads which have been coated with a high dielectric constant material (titania, zirconia). Recent studies evaluated efficiencies of both the PNL-developed corona reactor and a pulsed high voltage discharge system developed at LLNL. Reactor efficiency was determined for the reduction of NO/NO_2 and the combustion of propene (C_3H_6), an exhaust simulant, to CO_2.

In the propene oxidation experiments, an FTIR spectrometer was used to monitor the decrease in propene concentration and related increase in CO/CO_2 production in the gas stream from a packed bed reactor as a function of input power to the reactor and gas flow rate. Results for a packed bed reactor containing titania coated glass beads indicated that this system was effective for oxidizing propene. A relatively high CO_2/CO ratio was found, suggesting that a *clean-burn* had occurred. Zirconia coated beads showed a higher efficiency for oxidizing propene, however, the CO_2/CO ratio was lower. In addition, an increase in NOx was found for ZrO_2 coated beads. Crystalline phase and coating porosity are but two materials parameters which need to be investigated in future work along with the role of water vapor in the emissions destruction chemistry. The presence of a high dielectric constant oxide coating on the packed beads appears to catalyze olefin destruction. The mechanism underlying this observation is not yet established; however, it may be related to photocatalytic activity which is induced by light emission from the plasma.

Photocatalysis

The second approach was based on the photolytic activity of a thin film oxide, such as the anatase phase of titania (TiO_2) or the more chemically robust tetragonal phase of zirconia (ZrO_2). Ultraviolet irradiation of these materials at energies greater than the bandgap gives rise to the formation of electron-hole pairs. The hole sites (oxygen ion vacancies) are proposed to catalyze hydrocarbon oxidation reactions while the electron trap sites, corresponding to single charge reduced metal cations, would be effective sites to catalyze NOx reduction reactions. Irradiation wavelengths needed to induce charge separation range from 3.2 eV for titania to about 5 eV for zirconia. Such photon energies are easily achievable from battery powered light sources. Preliminary studies at PNL have established that hydrocarbon oxidation does indeed occur upon ultraviolet excitation of a titania film deposited on the inside of a flowing tube reactor through which a mixture of n-butane and air is passed.

A sol-gel dip-coating method has been developed and was used to deposit 40 nm thick anatase (TiO_2) films on both interior and exterior surfaces of glass capillary tubes. Homogeneous films deposited from highly acidic solutions transform above 250°C to an anatase phase of comparable density to sputter-deposited hard titania films.

Raman measurements confirmed the anatase phase and relative coating thickness. Approximately 150 capillary tubes (100 mm long, 0.7 mm inside diameter, 1.2 mm outside diameter) were packed in a honeycomb structure inside a quartz reaction tube and irradiated externally using a mercury lamp source. Butane oxidation to CO_2 in the presence of air was confirmed by means of gas chromatography. This experiment, which represents a 25-fold increase in surface area over the previous single tube experiment, confirmed the predicted increase in hydrocarbon reduction efficiency.

The effect of increased surface area and temperature on the catalytic efficiency still needs to be determined as does the efficiency for NOx destruction. The integration of fiber optic delivery systems to both localize the excitation and increase surface area are topics to be addressed in future work. Performance of a reactor based upon this technique also must be demonstrated at high exhaust gas flow rates.

Engel-Brewer Catalysts

Previous LDRD funded research has shown that porous, intermetallic thin foils with good structural and electrochemical properties could be produced using high-rate sputter deposition and vacuum annealing. Such materials were found to have excellent potential to replace precious metals (e.g., platinum) in many electrochemical or catalytic applications. The focus of FY 1994 research was to produce sufficient materials for detailed assessment of catalytic properties, and to examine alternative, less expensive, intermetallic systems. Three new sputter deposited films were produced and analyzed. Individual compounds were selected based on their expected high thermodynamic stability and potential for reasonable fracture toughness to ease fabrication. Generalized Lewis Acid-Base concepts were used to indicate thermodynamic stabilities in transition-metal compounds with crystal structures ($L1_2$ or B2) capable of polycrystalline slip at moderate temperatures. The first film was the iridium-niobium, $L1_2$ compound Ir_3Nb, which exhibited the best behavior in previous structural and electrochemical tests. This was followed by two B2 ruthenium deposits, RuTi and RuAl, which represent lower-cost and lower-density intermetallic alternatives. Scanning electron microscopy and x-ray diffraction analyses indicated that all deposits were within the target compositions and were single-phase $L1_2$ or B2 compounds. The Ru deposited films revealed a much rougher surface structure with RuTi exhibiting a porous microstructure even in the as-deposited condition.

Micro Heat Exchanger Development

Monte K. Drost (Analytic Sciences and Engineering)
Robert S. Wegeng (Process Technology and Engineered Systems)

Project Description

The objectives of this project were to develop a test apparatus for microscale phase change heat exchangers and develop and test high flux condensers and evaporators for heat pump and electronic cooling applications.

Experiments in FY 1993 suggested that it would be possible to develop microscale evaporators that can transfer up to 100 w/cm^2. The scope of work during FY 1994 focused on developing the ability to rigorously test microscale evaporators and to fabricate a number of test articles using a range of heat exchanger geometries.

Technical Accomplishments

The microchannel heat exchanger test loop was designed for use in experimental investigations of microchannel heat transfer and fluid mechanics. The operational capabilities of the loop were defined as flexibly as possible, so that the loop could be used to investigate a wide range of flow and heat transfer behavior, over as wide an operating range as possible. The loop design has also taken into consideration ease of modification, as new applications of microscale devices are developed and require testing. The initial design of the loop has been aimed at testing to evaluate the performance of microscale heat exchangers, since this is an application of microtechnology currently under development. But the loop will also be used for flow visualization studies and investigations to fully characterize the boiling curve on the microscale. It is intended that the design of the loop can be easily altered as needed to accommodate testing of innovative ideas for devices utilizing microscale fluid flow and heat transfer.

The working fluids to be evaluated in these tests during FY 1995 are water and the refrigerant R-124. Tests with water will be run under single-phase conditions and low quality boiling only. Tests with R-124 will be run for both single- and two-phase flow conditions, and single-phase vapor. The nominal operating conditions of interest for testing are

- the system pressure
- the total flow rate in the microchannel device
- the thermal power that can be removed
- inlet subcooling.

Parameters that must be monitored, either as desired data or to control the loop operation, include

- fluid temperature at exit of the microchannel device

- inlet and exit temperatures for the heat removal heat exchanger

- wall temperatures in the microchannel device.

Instrumentation and components of the loop have been selected to function over the appropriate ranges of these parameters.

The loop configuration is shown in detail in the diagram in Figure 1. It consists of three main sections; the primary circulation loop, the test loop, and the secondary heat removal loop. The primary circulation loop is used to pressurize the system to the desired operating pressure, and provides the driving pressure drop for the test loop. The working fluid (which may be water or R-124) is circulated in this loop at a relatively high flow rate, on the order of 2.5 to 3 L/min. The flow in the test loop is generally a very small fraction of this, varying from a few milliliters per minute up to around 1 L/min.

The working fluid in the secondary loop is always single-phase liquid water, with flow rate variable from approximately 30 mL/min to 1.8 L/min, depending on the heat removal requirements for a given test.

The main accomplishment of FY 1994 has been to assemble the loop and begin preliminary check-out tests. Three test articles, with Ti film heaters on the back side, and RTD instrumentation, have been constructed. The microchannels in these test articles were etched using ion-beam etching; two of them have an array of parallel channels, and one is a diamond-pattern array of fins (see Figure 2).

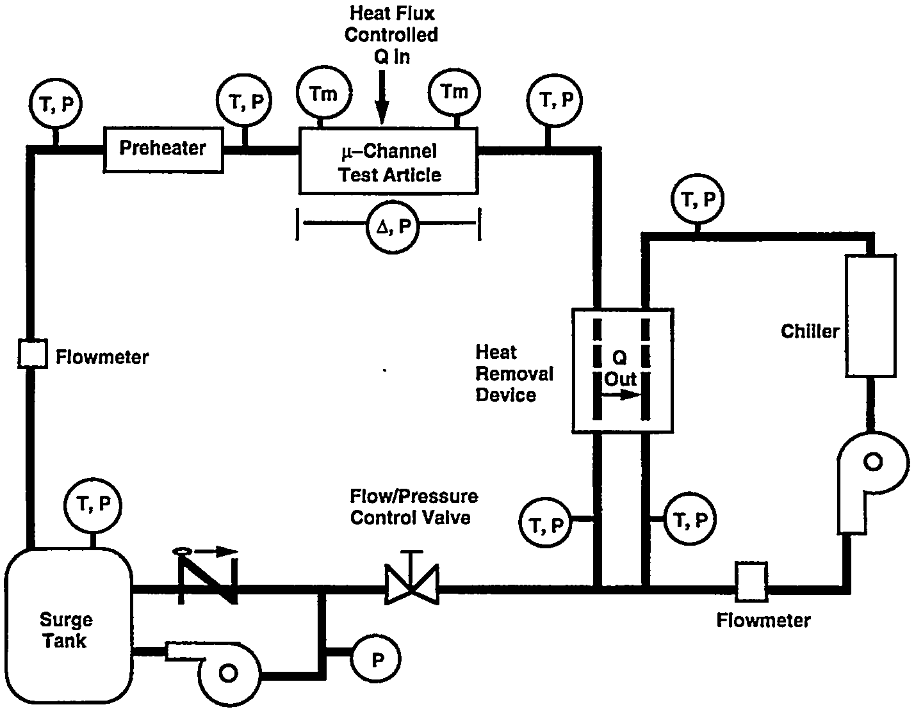


Figure 1. Micro Heat Pump - Flow Diagram

Figure 2. Micro Heat Exchanger

Microcompressor Development

Monte K. Drost (Analytic Sciences and Engineering)
Robert S. Wegeng (Process Technology and Engineered Systems)

Project Description

The objective of this project was to screen microscale compressor concepts and select one for a proof-of-principle test.

Technical Accomplishments

Compressor screening involved the identification of a range of options for providing microscale compression. Concepts included piezoelectric, electromagnetic, thermopneumatic, and acoustic and chemical compression. Performance calculations were completed on piezoelectric, electromagnetic, thermopneumatic, and acoustic compression. The results showed that piezoelectric, thermopneumatic, and electromagnetic concepts had theoretical efficiencies that could allow the development of a useful microscale heat pump. The acoustic concept appeared to be unattractive and was not considered further.

While three compressor concepts could provide useful compression, the electromagnetic concept appeared to have the highest theoretical efficiency and potential for development. Therefore, the electromagnetic concept was selected for further investigation.

A unique design of an electromagnetic compressor was developed. Performance calculations suggested that the electromagnetic prime mover could theoretically achieve an efficiency of 90% when viscous losses and joule heating were considered. A proof-of-principle demonstration of the unique concept was successfully completed in FY 1994.

Microscale Sheet Architecture Prototype Development

Monte K. Drost (Analytic Sciences and Engineering)
Robert S. Wegeng (Process Technology and Engineered Systems)

Project Description

The objective of the sheet architecture task was to 1) complete a closed loop test of a microtechnology based heat pump; 2) complete a prototype sheet heat pump which included all components except the compressor; 3) conduct a workshop on energy applications of microtechnology; and 4) investigate options for including the sheet heat pump in heating, ventilating, and air conditioning systems.

Technical Accomplishments

The closed loop test involved coupling a macroscale compressor to microscale evaporators and condensers to demonstrate a closed loop heat pump using microscale heat exchangers. The smallest available macroscale compressor required that approximately 90% of the refrigerant flow bypass the microscale condensers and evaporators. Assembly of the closed loop test was completed in FY 1994.

The prototype sheet heat pump task involved the fabrication of a 2 cm by 2 cm device that included a sheet microscale evaporator, an insulating material, a microscale condenser, an expansion valve, and appropriate flow channels for moving refrigerant between components. The evaporator, insulating material, and the sheet condenser were bonded together to form a prototype sheet heat pump. The prototype included all of the components of a heat pump except for the compressor. Two prototypes were completed in FY 1994.

A workshop on microtechnology for energy applications was organized as part of the sheet architecture task. The workshop involved 25 experts on energy utilization and microtechnology who were directed to identify attractive options for applying microtechnology to energy applications and to identify key research needs. The workshop recommended that future research focus on distributed energy applications, sensor, and power electronics applications of microtechnology.

Two options were identified for including a sheet vapor compression cycle heat pump in a building heating, ventilating, and cooling system. The first involved imbedding the sheet heat pump in the walls of a building while the second concept involved a package unit installed between the joists on the outside perimeter of the residence. The package unit can conveniently include forced convection for removing thermal energy from the heat pump and disposal of condensation. Conceptual designs were prepared for both approaches.

Publication

R. S. Wegeng and M. K. Drost. 1994. "Energy Systems Miniaturization." In *Mechanical Engineering*, American Society of Mechanical Engineers.

Presentation

M. K. Drost, M. R. Beckette, and R. S. Wegeng. 1994. "Thermodynamic Evaluation of A Microscale Heat Pump." Presented at the 1994 ASME Winter Annual Meeting.

Motor/Machinery Failure by Holographic Processing of Acoustic Signatures

Wayne M. Lechelt and Ronald H. Severtsen (Automation and Measurement Sciences)

Project Description

The prediction and detection of motor/machinery failures has been an ongoing problem in production facilities. A technology capable of evaluating motors/machinery without affecting normal plant operation would reduce problem diagnosis and maintenance costs. The analysis of acoustic signatures using non-contacting holographic image processing is one such technology and was the objective of this project.

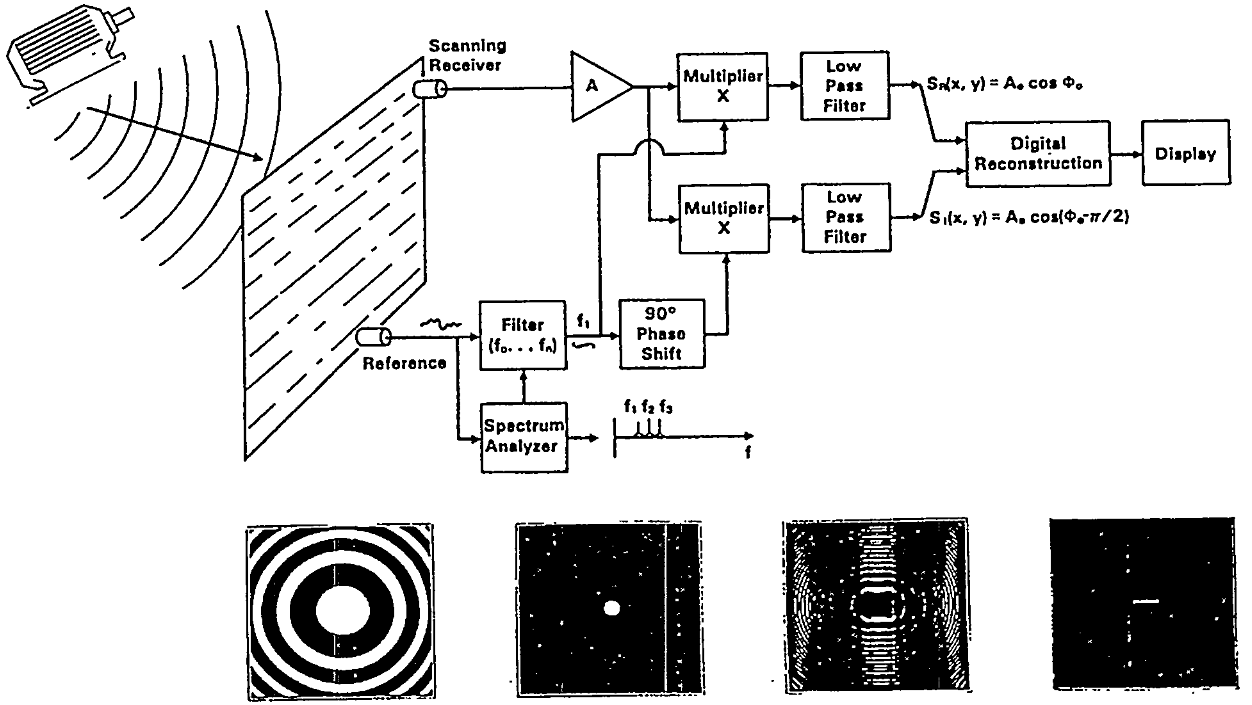
Technical Accomplishments

Acoustic signatures of different electric motors with good and defective bearings were holographically processed. The holograms of good and defective bearings were compared to determine the critical imaging parameters such as frequency, dynamic range, and scan aperture.

The critical imaging parameters for a holographic acoustic signature were

Aperture size	50 cm x 50 cm
Frequency range	2 KHz to 10 KHz
Dynamic range	100 db.

Three different types of electric motors were evaluated during the course of this project. Holograms of their acoustic signatures were generated. From these holograms the motors with good bearings could be distinguished from motors with defective bearings. Each motor type had a unique acoustic signature and resulting hologram.



Hologram of Point Source (f_1) Image of Point Source (f_1) Hologram of Line Source (f_2) Image of Line Source (f_2)

Passive Radiated Noise Holographic Imaging System

Off-Peak Cooling by Direct-Contact, Open- and Closed-Cycle Ice Making

Peter R. Armstrong and Michele Friedrich (Analytical Sciences and Engineering)

Project Description

The temperature drop across the ice-covered evaporator is an important factor in the cost and efficiency of a conventional ice-based off-peak cooling system. This project was motivated by an idea for eliminating the evaporator temperature drop. The objective was to establish preliminary feasibility of making ice directly from water, using water as the refrigerant, in order to achieve efficient, environmentally benign, off-peak air conditioning.

Technical Accomplishments

Literature Review

A number of direct freeze processes were explored in the 1950s for freeze-desalination: conventional surface freezing, direct contact with an immiscible refrigerant, flash freezing cycle with mechanical compression of water vapor, and flash freezing with absorption-desorption of water vapor. The second and third of these processes were demonstrated at pilot-scale but never implemented as full-scale plants; the overall economics of distillation and reverse-osmosis were apparently found to have a slight edge. Advanced absorption cycles have been under intense development in the last decade. Research has also focused on other advanced cycles, as well as on reexamination of older ideas that have lain dormant since simple vapor-compression cycles with chlorofluorocarbon refrigerants became the norm.

Ideal Cycle Analysis

The ideal cycle efficiencies of water (H_2O), ammonia (NH_3), and a chlorofluorocarbon refrigerant, R-12, were compared for various saturation cycles to produce a cooling effect at 0°C with heat rejection at 25°C, 30°C, 35°C, and 40°C condensing temperatures. Ten energy-efficient vapor-compression cycles involving multistage compression, multistage throttling, intercooling, and liquid injection were evaluated. The cycles were selected to be feasible (most have been used commercially) and to exploit one or more of the thermodynamic properties commonly considered in the selection of working fluids. The standard cycle yielded the poorest performance and a two-stage cycle with flash subcooling between throttling stages and liquid injection in both compression stages yielded the best performance. In the configurations that performed well for all refrigerants, water actually performed better than either ammonia or R-12. Water also performed exceptionally well in one of the simplest nonstandard cycles which uses single-stage compression and throttling with liquid injection to desuperheat the vapor as it is compressed. The performance of the two cycles with exceptional performance are compared to the standard cycle in Figure 1.

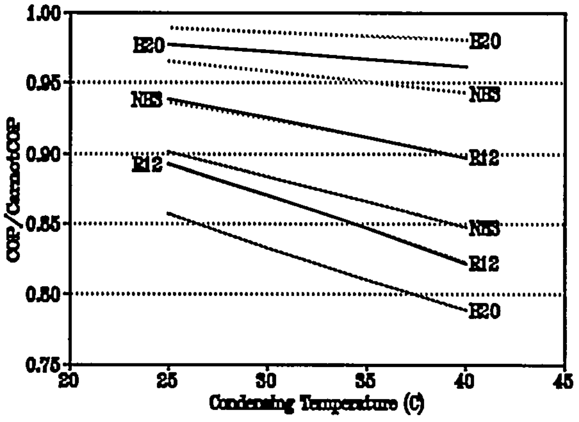


Figure 1. Ideal cycle efficiencies of three refrigerants in the best performing multistage (dotted) and single-stage (solid) cycles and in a standard (dashed) cycle.

Advanced Concept Development

While water has good ideal-cycle performance, its low density and high saturation pressure ratio at the temperatures of interest, together with the tendency for water-oil mixtures to emulsify, impose severe compressor design challenges. A handful of prototype centrifugal compressors have been built abroad for flash freezing of water in low pressure ratio (0.005 atm evaporating, 0.007 atm condensing) applications. The centrifugal compressor is only suitable for very large-scale applications because of the high tip speed required.

Synthesis of a number of ideas led to a novel oil-less compressor design suitable for small- to medium-scale applications.

A family of hybrid cycle machines, which can make ice using any combination of mechanical and thermal power, were also conceived. Such machines could give facilities with large cooling loads considerable flexibility in dynamic fuel selection.

Preliminary Market Study

The absorption-cycle based concepts are of particular interest in view of the recent and anticipated continuing market growth for non-chlorofluorocarbon cooling technologies. An absorption cycle with ice production could reduce the high first cost associated with absorption cooling which is currently one of the largest restraints on growth of this market. The market for absorption-cycle based off-peak cooling is likely to approach $500 million/year by 2010.

Applications

Large office or multibuilding cooling plants are currently the primary market for conventional off-peak cool storage systems. There are, however, a number of other potentially important applications. The annual cycle energy system (ACES)—an ice storage-based residential heating and cooling scheme developed in the 1970s—suffered from low heating/charging mode efficiency due, in part, to heat transfer resistance and from the high cost of it ice-making heat exchanger. These problems are eliminated when water is used as the refrigerant. Absorption- and hybrid-cycle ice-making concepts enable a variety of natural gas, waste heat, and multiple-power-source cooling applications ranging in size from residential to district cooling. In the large applications, ice slurry distribution and cogenerator-powered ice makers are natural fits. The reduced plant size afforded by thermal energy storage is an important factor in making absorption and hybrid plants cost-effective.

Demonstration

A simple flash-freezing apparatus was assembled to provide a desk-top demonstration of the direct-contact ice-making concept. The apparatus, consisting of a 1/3 hp vacuum pump, a standard Sporlan cartridge dryer, and a bell jar, appears in Figure 2. With about 5 g of water in the tray, boiling commences in 30 seconds and freezing of most of the water is accomplished in another 30 seconds. Water was also introduced from the top via a throttling valve to demonstrate the continuous ice-making process.

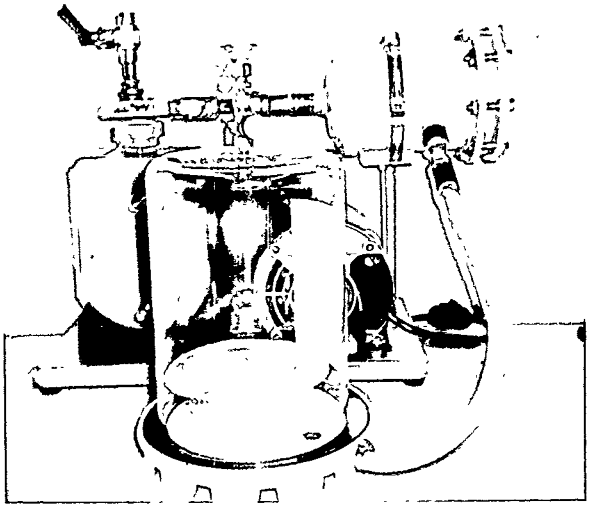


Figure 2. Vacuum Ice Demonstration Apparatus

Portable Dynamic Analysis and Design System

Daniel J. Trudnowski (Analytic Sciences and Engineering)

Projection Description

To reliably implement real-time control into power transmission systems will require significant technology advancements in many areas including engineering analysis and modeling of power system dynamics and real-time monitoring of the power system operating conditions. Over the last 3 years, PNL has been active in developing advanced techniques for analyzing measured and simulated power system response data. Early work focused on development of fundamental mathematical algorithms. These algorithms provided fundamental advances in power system dynamic modeling and analysis which enabled advances in several areas including advanced control system tuning and commissioning tests, tuning of generator controls, fault response studies to determine system dynamic characteristics, small-signal stability studies, and subsynchronous resonance analysis.

Technical Accomplishments

Efforts during FY 1994 focused on initiating development of a prototype PDADS unit, demonstrating applications of PDADS analysis techniques, and organizing a power system analysis and monitoring laboratory. The general frame for the PDADS has been defined and development work on the critical analysis components has been initiated. Demonstrations were conducted through collaborations with the U.S. Bureau of Reclamation on modeling hydro-turbine systems and the Bonneville Power Administration for field testing a thyristor controlled series capacitor.

A general architecture for PDADS has been established, and consists of three main components: 1) data collection and probing, 2) analysis, and 3) control system design. Software components of the system will be nonplatform dependent, which will maximize portability and flexibility, and the system will be completely compatible with BPA's portable power system monitor (PPSM). The software will be developed through integrated use of the software development system LabView, analysis software Matlab, and several PNL FORTRAN analysis codes. Data collection and probing functions will use technology compatible with LabView and will likely include an on-line digital signal processing (DSP) board.

The focus during FY 1994 was also on analysis and control system design components. Analysis functions are either time- or frequency-domain based. Prototype functions developed in LabView to date include periodogram averaging, Prony analysis, and several miscellaneous functions. Frequency-domain analysis functions prototyped to date include inverse discrete Fourier transform (IDFT) analysis, and plans have been developed for incorporating frequency-domain identification into the LabView interface. These analysis functions are being automated into LabView using the FORTRAN analysis codes developed in previous projects. The Matlab environment has been used for the control system design functions. Functions have been developed for automatically tuning lead/lag time constants given an identified model from the measured data. Also, functions have been developed for identifying open-loop system characteristics from measured closed-loop data. Such functions are of considerable value in tuning large-scale system controllers.

In June 1994, PDADS analysis capabilities were used during testing of the 500 kV thyristor controlled series capacitor (TCSC) recently installed in the BPA system. The TCSC is the first device of this type installed in a transmission system. It was built by the General Electric Company and installed in the BPA system as part of a major research project to assess the ability of such devices to enhance transmission system capacity. During testing, the TCSC was operated under many conditions creating significant effects in the northwest power system. The system response was measured using a time-synchronized wide-area monitoring system. PDADS was used to analyze the response data to determine the effectiveness of the device. In many cases, the analysis was conducted directly during TCSC testing providing immediate information to engineers.

A second PDADS application being developed is the tuning and modeling of power-plant generator controls. Accurate modeling of power plants is critical for engineering studies used to determine safe transmission loading conditions, and proper control of the power plant is required to maintain safe operation of the transmission system. Utilities put significant effort into properly operating and maintaining power-plant controls for transmission system performance.

FY 1994 results demonstrated advanced tuning and modeling of a hydro-turbine governor system at a power plant operated by the U.S. Bureau of Reclamation. A hydro-turbine governor system is often the most complicated system to model and control because its characteristics are nonlinear and dependent on the operating conditions of the plant. Experiments were conducted at the Blue Mesa power plant and PDADS was used to modify theoretical models to more accurately represent the actual behavior of the system. Without PDADS, development of an accurate model would require significant engineering time without guarantee of an acceptable result.

Publication

D. J. Trudnowski and J. C. Agee. "Identifying a Hydraulic-Turbine Model From Measured Field Data." Submitted to *IEEE Transactions on Energy Conversion*. The paper also will be presented at the 1995 IEEE Winter Power Meeting.

Prototype for Integrating the Total Energy Cycle

David M. Anderson (Environmental Management—TPAC)

Project Description

An objective of this project was to make significant improvements to the economic impact module of the energy/environment/economics (3E) life-cycle assessment prototype model that was constructed using LDRD funds during FY 1993. The life-cycle assessment prototype model featured an economic impact module that included a 10-sector static input-output model, which will estimate national-level economic impacts (employment, output, and income) given an economic shock scenario (a policy change). These include only direct and indirect effects, not induced effects. Therefore, we cannot estimate total economic impacts with the module in its current state.

This project addressed the most critical improvements in the module in order to facilitate a more complete life-cycle assessment capability. Specific improvements that were targeted for development in FY 1994 included constructing an induced-effects component to the impact estimation procedure, developing state-of-the-art input-output coefficients, providing the capability to perform subnational (regional) impact modeling, and an intensive peer review of the completed module.

Technical Accomplishments

All of the goals for this project were accomplished. The economic impact module of the energy/environment/economics life-cycle assessment prototype model was successfully modified to provide for regional economic modeling of any custom economic region in the country, while maintaining its capability to perform national analysis. The module was given an induced-effects component to allow theoretically sound economic impact estimation for regional economic models. A method to derive theoretical input-output coefficients that account for input substitution and technical innovation over time was developed and successfully tested. This econometric modeling work became the technical highlight of the project, and is a target of current peer-review efforts by the economics community.

As a technical highlight, the study resulted in the successful development of input-output coefficients which reflect 1) the responsiveness of industrial energy use to changes in prices; 2) static short-run energy substitution possibilities that arise from changes in the prices of other factors of production, namely capital, labor, and materials; and 3) longer-run dynamic energy substitution possibilities that arise from technological changes in manufacturing industries. The empirical development of input-output coefficients that reflect these determinants of industrial energy use provides an important tool for extending PNL's input-output capabilities to address a wider array of energy conservation and technological deployment issues.

Software was developed for linkage back to the life-cycle assessment prototype software developed in FY 1993 LDRD work. All of the module enhancements were added to the software, and "hooks" were embedded to allow any future enhancements to be plugged in. The software provides the interface for life-cycle assessment analysts to perform an integrated life-cycle assessment.

Publication

C. A. Ulibarri, W. Joerding, T. L. Marsh, D. M. Anderson. 1994. "Developing I-O Coefficients to Account for Substitution and Innovation: Is It the Chicken or the Egg?" In revision for submission to an econometrics peer-reviewed journal.

Presentation

S. A. Shankle, D. M. Anderson, K. K. Humphreys. 1994. "Integrating Energy, Economics, and the Environment: The Life-Cycle Assessment State of the Art." PNL-SA-24189. Presented at the 69th Annual Conference of the Western Economic Association International, Vancouver, British Columbia, June 29-July 3.

Pulsed Amplitude Synthesis and Control Development Converter Systems

Matthew K. Donnelly (Analytic Sciences and Engineering)

Project Description

The Pulse Amplitude Synthesis and Control (PASC) converter is a novel converter topology proposed to interface new generation and consumption technologies with the existing electric power network. In prior research, the converter has shown promise in the consolidation of diverse electrical sources into a single coherent alternating current waveform. The objectives of this project were to demonstrate the applicability of a novel static converter technology to contemporary power system problems and to build a prototype converter for testing and evaluation.

Technical Accomplishments

Fiscal year 1994 was the second year of funding on the PASC project. In FY 1993, we laid the theoretical framework for a PASC converter that could operate as a bidirectional interface between the utility electric power grid and isolated electrical devices. This work centered around computer studies using the complex Electro-Magnetic Transients Program (EMTP).

With FY 1993 as a foundation, we targeted two efforts for FY 1994. The first effort was the design and construction of a benchtop prototype. Dr. Don Hammerstrom, a power electronics specialist, was hired as a member of the project team and contributed substantially to the prototype development. With the majority of the construction completed on the 20 kW prototype, we experienced shipping delays with a key component. This was not seen as a major impediment since work continued on the controller design. We expect shipment of the MOS-Controlled Thyristors (MCTs) in the first quarter of FY 1995 at which time testing on the benchtop prototype will commence.

The second focus effort for FY 1994 was to assess PASC feasibility in an industry setting. Due to the unique consolidation features inherent in the PASC design, we chose the wind energy industry as a primary target. A staff exchange was initiated with R. Lynnette and Associates, a leading wind energy research and development firm. We developed and demonstrated economic evaluation software for the analysis of various wind farm design configurations. This software has generated interest from several wind energy firms. The software was used to perform a preliminary assessment of the economic feasibility of using a PASC design for a wind farm project in Goldendale, Washington.

Publication

M. K. Donnelly and R. J. Johnson. 1994. "Power System Applications for PASC Converter Systems." In *Proceedings of the 1994 IEEE T&D Conference*, Chicago, Illinois.

Screening Life-Cycle Assessment

Kenneth K. Humphreys and Scott L. Freeman (Energy and Industrial Analysis)

Program Description

Understanding the energy/environmental/economic (3E) impacts of energy technologies and how these change under varying scenarios is critical to DOE's ability to identify, develop, and deploy advanced energy technologies that are acceptable to the marketplace. Life-cycle assessment is a developing procedure that supports assessments of the 3E impacts of energy production and delivery systems from a "cradle-to-grave" perspective. The objective of this effort was to evaluate a technology that is early in the research and development process and attempt to understand the positive and negative 3E impacts that it will have once it is commercialized.

As part of the growing trend toward more responsible management of global energy and environmental resources, consumers and government agencies have been applying extreme pressure on the marketplace to produce products and technologies that are cost competitive, energy efficient, and environmentally benign. Life-cycle assessment has emerged as a prominent approach for evaluating the "cradle-to-grave" energy and environmental impacts associated with products and processes.

The following examples are clear indicators of growing industrial and governmental interest in life-cycle assessment:

- The Chairmen of the Chemical Manufacturers Association (CMA) has prominently advocated the use of life-cycle assessment techniques as a means for product and technology developers to protect the environment and become more competitive in the global marketplace.
- The International Standards Organization is developing life-cycle assessment standards that are expected to have sweeping implications for U.S. industry. (DOE is intending to revise its General Environmental Protection Orders in accordance with these new standards.)
- Two recently released Executive Orders and pending Congressional legislation address the application of life-cycle assessment in the federal sector (this includes the DOE laboratory system).

Although numerous U.S. companies are financing the development of life-cycle assessment methodologies for evaluating *existing* products and technologies, little effort has been put into methods to evaluate technologies early in the research and development process. (EPA reports that 80% of the environmental burdens associated with products and technologies are the direct result of decisions made early in the research and development process.)

Technical Accomplishments

As an initial attempt to develop a life-cycle assessment screening process for use early in the research and development process, a case study was conducted on a microtechnology heat pump used in residential applications. (Microtechnology heat pumps are under development at PNL under LDRD funding.)

The following life-cycle aspects of the microtechnology heat pump system were evaluated in the case study:

- Potential market penetration rates for microtechnology heat pumps in each U.S. geographic region and the associated energy-efficiency benefits of these penetrations.
- Reductions in selected pollutant loadings (e.g., NOx) associated with the microtechnology heat pump "cradle-to-grave" life-cycle (e.g., fuel extraction operations, fuel transportation, electricity generations, end-use).
- An evaluation (primarily qualitative) of the energy/ environmental/economic issues associated with microtechnology heat pump manufacturing versus conventional heat pump manufacturing.

This effort resulted in four products: 1) an initial life-cycle assessment screening approach that can be used to point to 3E problems associated with a technology early in the research and development process, 2) initial screening assessment results for a technology (microtechnology heat pumps) that are currently under development at PNL, and 3) increased staff capability for conducting life-cycle assessments.

Publication

K. K. Humphreys. 1994. "Life-Cycle Assessment: An Industrial Approach to Integrating Energy, the Environment, and Economics." PNL-SA-23528. Pacific Northwest Laboratory, Richland, Washington.

Superplastic Forming Aluminum Developed Multiwall Exhaust

Mark T. Smith and Curt A. Lavender (Materials Sciences)

Project Description

The objectives of this project were to continue the development of automotive superplastic aluminum materials and forming process capabilities and to demonstrate PNL's superplastic forming capabilities for lightweight vehicles.

Technical Accomplishments

This was the third year of the superplastic forming of aluminum project, with funding being focused on support of two new hires and transition of the project team from LDRD-supported research to funded project work. This transition was accomplished successfully, with a total of four funded superplastic forming projects currently at PNL.

Specific accomplishments during FY 1994 included the processing and testing of a new series of modified aluminum 5083 alloys. Test results for these materials showed significantly improved forming rates and superplastic elongations, and a Kaiser Aluminum produced version of this material was used by General Motors in a subsequent DOE-funded superplastic forming automotive door demonstration project. Elongations of over 475% were achieved during this work, and detailed microstructural analysis helped guide the development of the second phase of superplastic forming alloys that are now being developed on the NASA-funded Spitfire I program.

During the year, LDRD-funded work was also focused on development of improved laboratory testing capabilities. A new screw-driven tensile test frame having more accurate displacement control was prepared, and video-based extensometry has been incorporated into one of the test machines. Finally, a number of forming experiments were performed on the modified Al-5083 alloys to demonstrate formability differences between PNL's modified alloys and commercial superplastic forming materials.

Publications

C. A. Lavender and M. T. Smith. 1994. "Optimization of the Superplastic Behavior of 5XXX Aluminum Alloys." *Research Guidelines for Aluminum Product Applications in Transportation and Industry*. Eds. D. Weissman-Berman and E. Hay, ASME CRTD-Vol. 29, pp. 123.

C. A. Lavender, J. S. Vetrano, M. T. Smith, S. M. Bruemmer, and C. H. Hamilton. 1994. "Development of Superplasticity in 5083 Aluminum With Additions of Mn and Cr." International Conference on Superplasticity in Advanced Materials, Moscow, Russia (to be published by *Materials Forum*).

J. S. Vetrano, C. A. Lavender, and S. M. Bruemmer. 1994. "Impurity Segregation During Superplastic Deformation of Al-Mg-Mn Alloys." International Conference on Superplasticity in Advanced Materials, Moscow, Russia (to be published by *Materials Forum*).

J. S. Vetrano, C. A. Lavender, C. H. Hamilton, M. T. Smith, and S. M. Bruemmer. 1994. "Superplastic Behavior in a Commercial 5083 Aluminum Alloy." *Scripta Metallurgica* Vol. 30, pp. 565-570.

4.0 Other

4-DIVAS

David B. Rex (Information Systems and Engineering)

Project Description

4-DIVAS is an integrated four-dimensional (the standard three Euclidean dimensions and time) spatial information analysis and visualization system. The system integrates the AVS geometric visualization tool with persistent C++ objected-oriented data management class libraries and proprietary analysis modules. The resulting system permits interactive display, query, and analysis of spatially-related data in four dimensions. The data may be of either raster or vector origin, or both. This tool permits the evaluation and analysis of dynamic volumetric systems.

Technical Accomplishments

The syntax and grammar for the Spatio-Temporal Query Language was developed. The grammar allows a query to be couched in terms of bounding space and time for the volumetric data. Additionally, it provides for a delay factor in cases where the returning animation is displayed too fast for comprehension.

Because the funding was not adequate for the development of a command line parser, a query-by-form widget was developed for query entry. The user fills in the required information and then executes the query by pressing the "Execute" button.

Code modifications and new code amount to a little over 1000 lines of combined C and C++ code for the animated query module and the underlying socket data transfer code. The current state of the code is buggy, and the animated query module is currently not stable. The vendor supplying the database class library is shipping a new, improved version which should eliminate some of the current compile errors.

Presentations

D. B. Rex. 1994. Visualization '94. University of Utah, Salt Lake City.

D. B. Rex. 1994. National Center for Geographic Information Analysis (committee members) University of California, Santa Barbara.

D. B. Rex. 1994. GVIS 94, Richland ACM SIGGRAPH conference on Graphics and Visualization, Richland, Washington (extended abstract published in the conference proceedings).

A New Approach to Foreign Policy

Nancy M. Dowdy (National Security and Defense Planning—TPAC)

Project Description

The objective of this project was to develop a methodology for constructing and evaluating a foreign policy package for another country or region and to demonstrate its use by an illustrative example. The methodology would draw upon approaches from the Harvard Negotiating project, and take advantage of expertise at PNL in developing metrics for things that are not readily quantifiable and not directly comparable. It would fold in cultural values in evaluating approaches for a given

Historically, little integration has been attempted among U.S. government approaches to a given country in policy arenas assigned to different Executive Branch agencies, except where it was required because of a crosscutting issue. Today, we recognize the increasing interdependence among policy arenas (e.g., the economic factor in national security). Furthermore, incentives in unrelated areas are frequently being offered to persuade other countries to cooperate in areas of U.S. concern.

Formulating a good integrated foreign policy requires (at least) three things to be in place that are now lacking: 1) agreement on U.S. national goals and objectives regarding other countries, 2) a methodology for constructing and evaluating (in a timely way) foreign policy initiatives that promote U.S. objectives, and 3) an organizational structure within the government empowered to carry out the methodology and gain Presidential endorsement of chosen sets of options. This project seeks to define a methodology for constructing and evaluating integrated sets of foreign policy initiatives toward a given country or region that would be attractive to the other party, would yield a net benefit to the U.S. and the other party, and would support U.S. national goals.

Technical Accomplishments

In FY 1994, an eight-step process for developing and evaluating integrated foreign policy options was developed. The method begins with a clear U.S. objective and identifies functional drivers for the other party that, in essence, comprise the competing objectives of the partner. Ongoing and potential U.S. programs that address the partner's objectives are evaluated, and integrated policy options are selected with the aid of a simple graphical presentation. Sociopolitical and technological factors are taken into account, as appropriate, in determining the partner's objectives and evaluating programs.

The method provides an overall framework that ensures that the right questions are asked and would enable decision makers to digest the analyses to select good policy options.

Advanced Biomedical Science and Modeling

Richard W. Weller and Melvin R. Sikov (Biology and Chemistry)

Project Description

The purpose of this project is to explore applications of advanced technologies to biomedical problems. The project provides a logical progression of DOE's role in developing technological solutions to national concerns, and should lead to new means for detecting and evaluating potential health hazards associated with the work environment, as well as enhanced diagnostic and therapeutic modalities with broad applications. Integration of capabilities in physical, mathematical, and biomedical sciences, together with external collaborations, will allow substantive, innovative contributions.

Technical Accomplishments

Imaging to Detect and Diagnose Disease

Investigations of imaging by detection or spectroscopy of intrinsic/induced fluorescence and adaptive optical transmission in the near-infrared and the visible spectrum were conducted during FY 1994. Efforts were continued to identify and eliminate interfering spectral signatures so that the spectral properties of the cell lines could be unambiguously identified.

Collaborations suggested a novel approach for studying tumor cell behavior using peroxidase activity and aminomelanin (AM) and disoluminomelanin (DALM) synthesis. A prototypic cell line, HL-60, was cultured with 3-aminotyrosine (3-AT) which is the substrate for aminomelanin synthesis. Treated and control cells were harvested and excited at 355 nm. Increased emission in the spectral region with a modal 500 to 520 nm peak was observed in treated cells (Figure 1). Both treated and untreated cells fluoresce, but there are significant spectral differences. The aminomelanin approach was extended to a rat mammary tumor cell line grown ex vivo with similar results (Figure 2).

Quantification of Motility and Patterns

This task was initially directed toward the utilization of images to quantify movement in utero and throughout lifespan as a measure of well-being. Initial efforts were based on videotapes of human ultrasonic fetal examinations. A preliminary demonstration of feasibility was incorporated into a briefing at the U.S. Army Madigan Medical Center (MMC).

A second experiment was conducted to demonstrate the capability to acquire data from both a normal and an abnormal motion image sequence. In that experiment, tropical fish were imaged during normal motion using a standard video camera; the fish were then sedated by degrees and additional imaging was performed. A characteristic metric was defined so that the degradation of motility was shown graphically as a plot of motility versus degree of sedation. This demonstrated the potential for quantifying impairment of movement. A white paper was prepared describing the results of the video experiments. Software acquired in FY 1994 will be tested in FY 1995 to validate its usefulness in studies of human motion.

Staff efforts were then redirected to multimodality physical detection processes that were being conducted in conjunction with the spectral signature experiments. Images of transplanted rat mammary tumors were obtained using an Inframetrics thermal imaging camera that employs a mercury-cadmium telluride detector with an 8 to 12 micron response range. Tumor images were recorded on standard video output, digitized, and processed. We were able to detect tumors as small as 2 to 3 mm in diameter at depths of 1.5 to 2 cm below the surface of the skin. Analyses of the underlying readings, moreover, disclosed that the measured temperatures associated with the two-dimensional projections of the developing tumor were lower than those of surrounding areas. This finding was reproducible and suggests interesting associations between thermal conditions and angiogenesis that warrant exploration.

Enhanced Interpretation of Diagnostic Images

The focus of this work has been to maximize diagnostic image quality in order to increase the usable content and amount of information extractable from images. Methodologies developed during FY 1993 and direct and indirect digitization techniques are being used to enhance detection and diagnosis of disease through pattern recognition and/or textural analysis of images.

Images were obtained using standard video equipment and a digital camera. Comparison of images obtained by both methods showed the advantages of digital acquisition with image enhancement for object or feature recognition. The database created by this activity is being used to develop interactive computerized models and algorithms (i.e., neural networks) to facilitate diagnosis. Work conducted

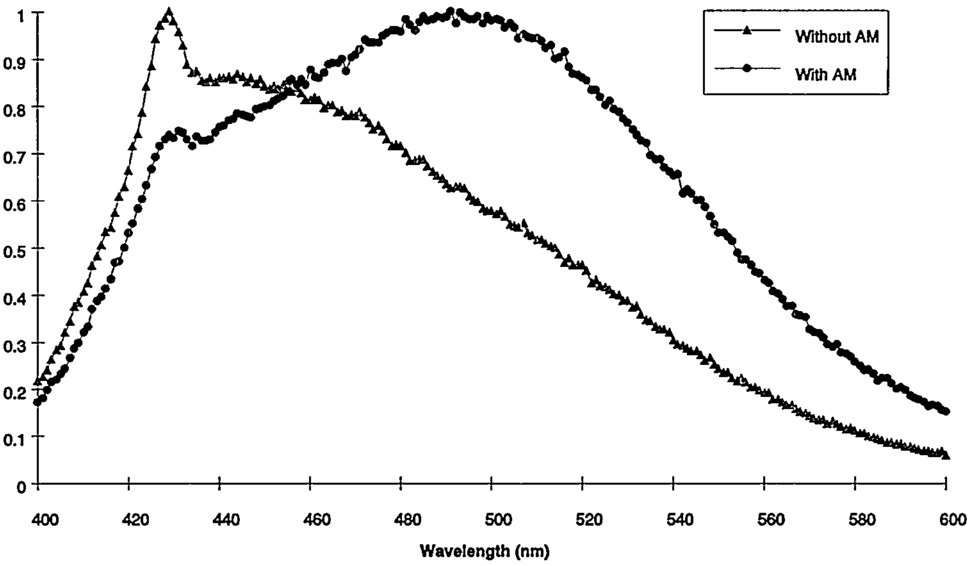


Figure 1. Increased emission in the spectral region with a Modal 500 to 520 nm peak was observed in treated cells.

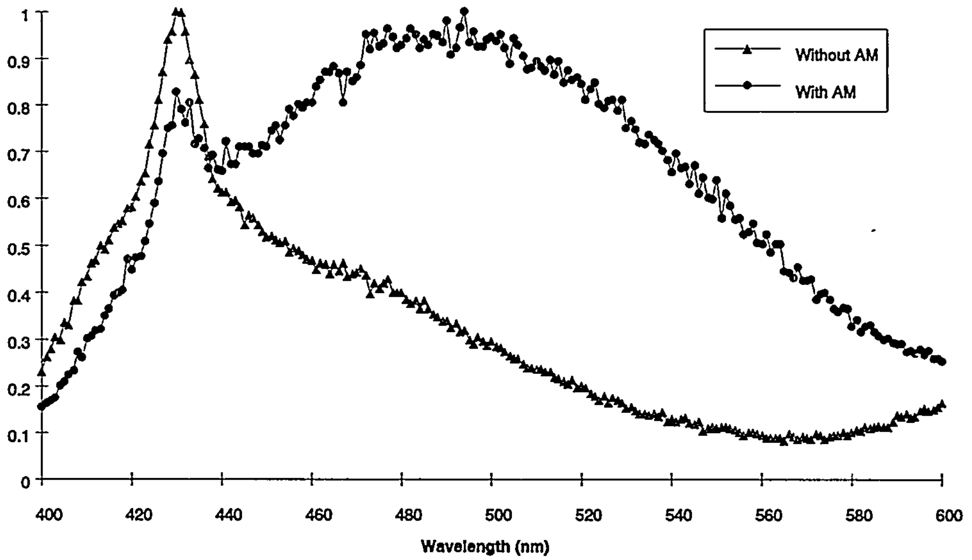


Figure 2. The aminomelanin approach was extended to a rat mammary tumor cell line grown ex vivo with similar results.

on this task enabled us to rapidly respond to an opportunity to collaborate with Sacred Heart Medical Center in Spokane, Washington. The collaboration involved processing and evaluating x-ray images to determine the feasibility of diagnosing catheter placement with an artificial neural network. Results suggested that an automated diagnostic tool could be developed.

Chemical Model of Cholelithiasis

This was a collaborative effort with Earth and Environmental Sciences and Life Sciences Centers to provide a basis for exploring the possibility that gallstone formation may be increased by dietary modifications introduced to avoid or respond to other diseases. In this past year, an in-depth, critical analysis of the pertinent literature identified those components of bile that have a high probability of being important indicators or factors in stone formation and, insofar as possible, the effect of disease, diet, and other physiological conditions on the production and concentrations of important components. The predictive model was compared to data obtained from the analysis of bile samples taken from the validated PNL animal model during a pilot study. That comparison was used to refine the model and identify critical analytes in blood and bile.

Publications

C. A. Pekow, R. E. Weller, B. B. Kimsey, and M. A. Allen. "Ultrasound-guided cholecystocentesis in the owl monkey." *Lab. Anim. Sci.* 44:365-368, 1994.

C. A. Pekow, R. E. Weller, S. J. Schulte, and S. P. Lee, "Dietary induction of cholesterol gallstones in the owl monkey: Preliminary findings in a new animal model." *Hepatology* (in press).

Presentation

C. A. Pekow, R. E. Weller, B. B. Kimsey, and M. A. Allen. "Ultrasound-guided cholecystocentesis in the owl monkey (*Aotus nancymae*)." American Association for Laboratory Animal Science Annual Meeting, Nashville, Tennessee, November 1993. Abstract and poster presentation.

Boiling Water Reactor (BWR) Advanced Fuels

Bruce D. Reid, Edward F. Love, Andrew W. Prichard, and Sandra L. Harms (Safety and Performance Analysis)

Project Description

An initial evaluation of several advanced boiling water reactor fuel products has been started. The objective of this project was to further develop and evaluate these fuel products to identify potential energy efficiency improvements, which would result in a cost savings to nuclear utilities.

Technical Accomplishments

Three separate concepts were identified as having the potential to provide benefit to existing boiling water reactor fuel assemblies. Neutronic code models have been developed to determine the technical feasibility of these concepts. A brief description of the three advanced boiling water reactor fuel product concepts follows:

1. To improve fuel utilization in the upper regions of a boiling water reactor core, a spectral shift insert component (SSIC) that could be inserted into the lower region of a boiling water reactor bundle was devised.

2. A boiling water reactor solid moderator concept was devised to improve fuel utilization in the upper regions of a boiling water reactor core.

3. A burnable absorber coating concept is being studied in an effort to remove lumped burnable poisons from boiling water reactor bundles.

Each of the three concepts has the potential to provide improved neutronic efficiency and fuel performance capability.

Computational Modeling of Complex Physical Systems Initiative

Rik J. Littlefield (Analytic Sciences and Engineering)
Steven B. Yabusaki (Earth and Environmental Sciences)

Project Description

The objective of this project was to develop state-of-the-art computational modeling capabilities, particularly utilizing highly parallel computer systems, and to demonstrate the resulting capabilities through application to scientifically important and highly technically challenging problems. Successful completion will provide for a greatly enhanced modeling capability in a variety of application domains, including coupled atmospheric transport and chemistry, subsurface transport, coupled heat and mass transfer phenomena, and fundamental fluid dynamics phenomena. In addition, it will develop expertise in parallel computational modeling that can be applied to further scientific domains as required.

Technical Accomplishments

Accomplishments for FY 1994 include the following:

- Development of parallel software to support, and completion of, a Direct Numerical Simulation study of cell formation and turbulence states in a double-pane window, involving 2.4 million degrees of freedom and 78,000 time steps. This research has spawned involvement of the principal investigator in other large-scale parallel modeling projects, in particular parallelizing the Oceanic Large Eddy Model.
- Development of a massively parallel version of the PNL-Watershed code to assess the impact of global warming on the Columbia River watershed. Some of these results are now being used to support the Columbia River Watershed Analysis project under Global Studies.
- Development of a massively parallel code for modeling subsurface flow and transport in aquifers with multiscale material heterogeneities. This code was used to study permeability scaling behavior in geologically complex groundwater systems.
- Development of a parallelized version of GChM. This code was used to analyze temporal and spatial distributions of global carbon monoxide compared with space shuttle data.
- Development of a domain-decomposed version of parallel TEMPEST, which executes both on highly parallel supercomputers (Intel Paragon) and on multi-processor and clusters of high-end workstation computers (Hewlett Packard, SGI Reality Engine, and SGI Power Challenge). Development and evaluation of several numerical methods included implementation of a library of iterative sparse linear system colvers: tfqmr, bicgstab, bicgs, minres, and multiplicative Schwarz; implementation and evaluation of block ADI, diagonal, and multi-level preconditioners to accelerate convergence of the iterative solution methods, and development of a real-time interactive visualization capability that works with the parallel TEMPEST.

Publications

J. R. Phillips. 1994. "Simulation of Turbulent Flow in Unstratified Double Pane Windows." *Bulletin of the American Physical Society* (in press).

J. R. Phillips. 1994. "Simulation of turbulent flow in unstratified double pane windows using the Intel Delta Computer." CSCC Annual Report, Caltech (in press).

R. D. Saylor, R. C. Easter, and E. G. Chapman. "Analysis of mid-tropospheric carbon monoxide data using a three-dimensional global atmospheric chemistry numerical model." In *Air Pollution Modeling and Its Application X*, eds. S.-E. Gryning and M. Millan. Plenum Publishing Corp., New York (in press).

T. D. Scheibe and S. B. Yabusaki. "Scaling of flow and transport behavior in heterogeneous groundwater systems." *Water Resources Research* (to be submitted).

Presentations

R. C. Easter, R. D. Saylor, and E. G. Chapman. 1994. "Analysis of mid-tropospheric carbon monoxide data using a three-dimensional global atmospheric chemistry model." American Meteorological Society Conference on Atmospheric Chemistry, Nashville, Tennessee, January 23-28.

R. D. Saylor, R. C. Easter, and E. G. Chapman. 1993. "Analysis of MAPS carbon monoxide data using a global atmospheric chemistry numerical model." Paul Crutzen Symposium on Challenges in Atmospheric Chemistry and Global Change: Yesterday, Today and Tomorrow, Boulder, Colorado, December 2-4.

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T. D. Scheibe and S. B. Yabusaki. 1994. "Permeability scaling in a numerical aquifer." AGU Chapman Conference on Hydrogeologic Processes: Building and Testing Atomistic- to Basin-Scale Models, Lincoln, New Hampshire, June.

T. D. Scheibe and S. B. Yabusaki. 1994. "Visualization of transport in heterogeneous porous media." Geological Society of America Annual Meeting, Seattle, Washington, October 24-27.

S. B. Yabusaki and T. D. Scheibe. 1993. "Scaling of flow and transport behavior in heterogeneous groundwater systems." (Abstract) *EOS Trans. AGU*, 74(43):251, video poster presented at the American Geophysical Union Fall Meeting, San Francisco, California, December.

Computer Intensive Methods of Hypothesis Testing

Robert F. O'Brien (Analytic Sciences and Engineering)

Project Description

Existing statistical methods of testing environmental pollution monitoring and environmental cleanup efforts use classical parametric and non-parametric tests to assess environmental change. These tests all require certain design assumptions such that there exists a random sample of observations from a cleanup site to make inference to the site in general, independence of the sample observations, and that the observations be identically distributed. However, in environmental sampling, these assumptions are not met or are difficult to validate. The purpose of this research was to develop computer intensive statistical hypothesis testing methods that were more robust to naturally occurring environmental conditions.

During FY 1994, research focused on the development and application of the computer intensive method of randomization testing techniques to environmental situations.

The objective was to develop improved statistical methods for dealing with environmental pollution monitoring that are reliable, defensible, and meet actual problems of concern in environmental restoration. We plan to achieve this objective by

- comparing randomization and bootstrapping methods to classical tests used on past environmental data sets
- developing software routines that ultimately can be packaged for use by non-statisticians in environmental restoration.

Technical Accomplishments

A thorough literature review was accomplished on randomization and bootstrapping methods in the relevant statistical and environmental literature. From this literature search appropriate computer algorithms were developed for executing the randomization and bootstrapping techniques and developing a suite of statistics that would be of interest in environmental remediation.

Initial data sets were gathered and custom programs were developed to analyze these data sets. Results indicated that these computer intensive methods are viable alternatives for environmental restoration when distribution of the test statistic is unknown or has no closed form mathematical representation.

The development of generalized computer code is still ongoing, and will be funded in FY 1995 programmatically. Other data sets will be gathered to develop a broader application of computer intensive methods of testing environmental data.

CW Molecular Discriminator

Richard C. Hanlen and Wes L. Nicholson (Technology Research)
Jacqueline E. Madison (Technical Information)

Project Description

The objective of this project was to develop a methodology that describes and discriminates between chemical weapons agents and other toxic chemical agents. The suggested approach was to first generate a list of properties for known chemical weapons agents. The list would include the molecular structure, descriptive properties, and chemical/physical properties. The same exercise would be repeated for all known pesticides, herbicides, and fungicides. A mathematical description of the molecular structure would be added for each agent. Then, classical multidimensional clustering techniques would be used to construct a discrimination function on the space of all properties. The data would be extracted from computerized databases available through the PNL technical library.

Early efforts on the project brought forth several issues which made it very clear that the original objective would be extremely difficult to accomplish and clearly impossible with the available limited funds. These issues include

- the potential role of formal organic chemistry
- the identification of chemical weapons agents as opposed to toxic chemicals in general
- the complexity and non-uniformity of data presentation in retrievals from computerized databases.

The chemical weapons molecular discriminator proposal thesis that appropriate quantitative treatment of data available in the literature would help to discriminate chemical weapons agents from other chemicals is judged to be naive and unproductive by some members of the EMSL technical staff. The feeling is that nothing productive could be accomplished without knowledge of and introduction of a large body of formal chemistry that relates molecular structure and chemical properties to effects on living organisms.

Chemical weapons agents are not necessarily more lethal than pesticides, fungicides, and herbicides. Other considerations surrounding the logistics of field operations are probably as important as lethality in selection of chemical weapons agents. Is the agent easy to transport and distribute? What is the normal residence time? Does the agent deposit out, stay airborne in the vicinity, or waft away on the first gust of wind? Thus any useful scale of chemical weapons potential must involve much more than lethality. Another consideration is that for many chemical agents lethality information is more qualitative than quantitative.

Quantitative estimates result from either formal experiment or happenstance incident and are attached to specific doses. Without a quantitative scale, agents are difficult to rank with respect to lethality.

Computerized databases do not have uniform formatting. Hence retrievals tend to be verbose in the sense that key words that generate the retrieval are interspersed among modifying information. Also retrievals include symbols and spacing for aesthetics that complicate the description of unique strings that locate the information of interest. Thus extraction of the desired information into a form usable for input to an analysis package is very complex.

The above three issues suggest that a modified scope might produce a useful LDRD product, first as a beginnings toward chemical weapons agent discrimination and second, in a more general context, as a tutorial on ideas and tools for

1. extracting specific quantitative information from computerized databases
2. editing and reformatting the extracted records
3. developing code to input such records into an appropriate statistical analysis package.

Technical Accomplishments

In FY 1993, data was extracted by the PNL Technical Library from various sources. In FY 1994, we compiled the data and developed some of the tools described above for extracting, editing, and reformatting records so that they could be placed into a statistical analysis package. Using the tools, chemical formulas for fungicides, herbicides, and pesticides were studied. Interviews were also conducted with members of the EMSL staff to determine the viability for this task. A report is being generated that describes these tools and the analysis.

While no further work is planned, the results suggest that the wealth of information in computerized chemical databases can be efficiently and economically scanned, selectively extracted, organized, and fused for computer analysis. Thus, large sample distributional answers are tractable for questions in chemistry.

Development of Laser-Diode Based Sensors for Trace Isotope Assays

Bret D. Cannon, James F. Kelly, and Charles A. Whitehead (Chemical Sciences)

Project Description

The objective of this project was to demonstrate feasibility of a portable isotopic assay instrument for sub-nanogram amounts of metal elements based on laser-diodes light sources combined with graphite-furnace atomic absorption. This technology will be particularly suitable for detecting proliferation effluents and could be used in the field to support onsite inspections for treaty verification. Laser-diodes, developed for communications, consumer electronics, and other mass markets, can optically resolve isotopes using Doppler-free saturated absorption, and with laser-diodes, portable saturated absorption systems can be designed that require limited technical expertise to operate. Such isotopic assay instruments will permit use of isotope dilution to provide absolute quantification for graphite furnace atomic absorption without the exacting work of preparing calibration standards that are exactly matched to the samples to be measured.

Technical Accomplishments

A variety of agencies monitoring proliferation and/or waste remediation would benefit from portable assay equipment that gives accurate elemental and isotopic abundance information in the field. Such a device would need to be sensitive to atomic analytes at the sub-nanogram level, provide well-resolved isotopic determinations, and offer simple sample preparation with reliable measurement of absolute concentrations. Measurement of isotopic abundance information allows isotope dilution to be used to easily and accurately determine absolute concentrations. This project demonstrated that Doppler-free atomic absorption in a graphite furnace atomizer using saturated absorption with radio-frequency-modulated laser-diodes and heterodyne detection can meet these needs. Heterodyne detection of radio-frequency-modulated laser light improves the minimum detectible absorption by factors of 100 to 10,000 over conventional absorption techniques. Laser-diodes are small, rugged, and reliable light sources that are suitable for atomic absorption measurements with many elements including U, Ba, Cs, Rb, Li, K, Pu, and many lanthanides. The recent commercial introduction of laser-diode sources emitting near 430 nm adds Ca, Tc, and Cr to this list of elements. The marketing of sources based on the second harmonic of other commercially available laser-diodes would permit micro-assays of most other metals.

Work during FY 1994 included setting up and characterizing the apparatus. A vacuum system containing a commercial graphite furnace and windows to allow laser beams to pass though the center of the furnace was assembled and tested. The vacuum system allows control of the pressure and composition of the gas within the furnace, which is needed to obtain isotopic resolution and high sensitivity. The furnace reaches a maximum temperature of 2500°C and should be able to reach 3000°C with a larger power supply. Optics for the saturated absorption were set up and the laser beams aligned through the graphite furnace and also into a high-resolution wavelength meter.

A single-frequency laser-diode was locked in wavelength to a strong transition from the ground state of uranium. Radio-frequency modulation of this laser-diode was then characterized using two different modulation techniques. An external electro-optic modulator was used first and low modulation depth was obtained. With direct modulation of the current through the laser-diode, the modulation efficiency varied greatly with modulation frequency presumably due to impedance matching variations caused by parasitic capacitance and inductance, so that modulation sidebands are reduced by a factor of 2 when the modulation frequency is changed by 10 MHz to either side of the optimum. Large modulation was obtained near 140 MHz with one milliwatt of radio-frequency power. Analysis of the heterodyne signal from the detector with a radio-frequency spectrum analyzer showed that direct laser-diode modulation should allow minimum detectable absorbances of 10^{-6}.

As the last step before looking for uranium absorptions in the graphite furnace, we failed in our attempt to wavelength lock the radio-frequency-modulated diode laser to a uranium absorption. In September, while replacing the computer controlling the high-resolution wavelength meter, an old version of the software was loaded which resulted in inaccurate wavelength readings and hence not finding the uranium absorption. This problem was fixed and with additional funding for FY 1995 this work will proceed.

Electronic Information Space for Molecular Science Research

David M. DeVaney (Information Systems and Engineering)

Project Description

The objective of this project was to enhance PNL's ability to use World Wide Web (WWW) communication technologies to strategic advantage in sharing scientific information with collaborators, colleagues, and customers. Information included reports, papers, images, information about Environmental Molecular Sciences Laboratory (EMSL) computational and experimental resources, and ideas for future research. The project provides a demonstration of World Wide Web capabilities to create an electronic information space that can be easily navigated, and that improve PNL's World Wide Web service so that it is easier and more efficient to manage and operate. Specific accomplishments include development of a paradigm centered around a graphical view of the information being presented, investigation of full text searching for locating documents of interest and information within documents, and exploration and development of techniques for converting documents to World Wide Web's HyperText Markup Language (HTML).

Technical Accomplishments

Experience the Visible Results

Navigation of the World Wide Web pages is the best method for appreciating the value of this project. Because time did not permit clearance of all information developed, these pages are currently available only internal to PNL (private pages). However, the EMSL project plans to use these results to influence and support World Wide Web information distribution and in the near future we expect this to be apparent to World Wide Web navigators who reach EMSL public pages after arriving at http://www.pnl.gov:2080. Select visitors and PNL staff can see the full write-up of the project and its results on EMSL's private World Wide Web pages when they are on (or logged on through the security firewall) PNL's Local Area Network.

Graphical Information Spaces

The biggest gain in information presentation may be in the departure from the textual paradigm, in favor of a paradigm centered around a graphical view of the information being presented. If information is organized to place related information in a visually relevant context, with some background image relating to the type of information presented, the relationships and location of data may be better retained. In developing a graphical paradigm for information browsing, a significant part of our effort was invested in an artistic endeavor to capture the essence of the information contexts for EMSL. Figures 1 and 2 provide examples of this effort. Users of the World Wide Web pages resulting from this project can navigate to a large variety of diverse EMSL information by clicking on relevant portions of these graphical images. Although HTML provides for making graphical images active parts of a hypertext document (the ISMAP protocol), lack of available tools for processing an image made this a labor-intensive task. To enable efficient creation and maintenance of graphical World Wide Web pages by researchers and support personnel, we developed a simple first generational tool (HotSpot) to easily create hypertext markup (ISMAP) of images. HotSpot was developed with a Mosaic-based interface for UNIX workstations. Using HotSpot, the images in Figures 1 and 2 are easily marked up with hypertextually sensitive areas (circles and rectangles) that will respond to an information browser's mouse clicks. In HotSpot, the boundaries of these areas are made visible, but the ISMAP approach does not provide the user a way to determine what area is active; the assumption is that any visually interesting area will be responsive. To avoid confusion, we provided a default null response on our images; a short beep is provided for mouse clicks on inactive regions of an image. Figure 3 is a standard graphical navigation image that occurs consistently at the bottom of these World Wide Web pages to provide continuity of context and familiarity of navigation capability for the user.

EMSL staff and their collaborators on the World Wide Web will be able to search by visual context for relevant documents published in the EMSL information space.

Full Text Searching

It was necessary only to locate and select from available tools and demonstrate the ready viability of this technology. Many of the best tools are not yet available commercially and neither installation nor use is simple and straightforward. This aspect of the project focused on encouraging and enabling user/developers and maintainers of World Wide Web pages (i.e., HTML documents) to take advantage of such tools in publishing information on World Wide Web.

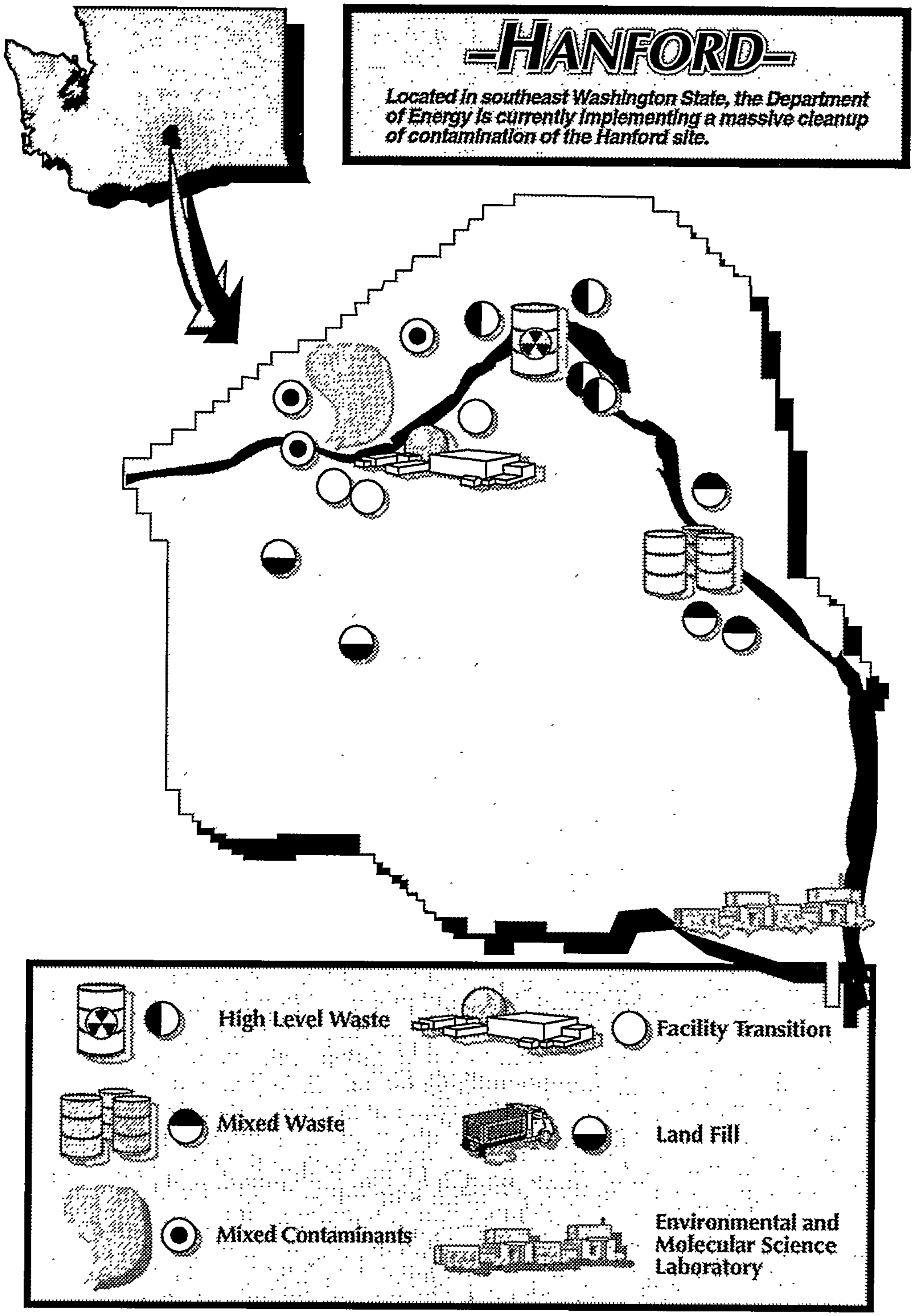


Figure 1. Hanford Site Map

There was no tool available that provided a single level of text search that could select from among many documents and also find text within a document. A two-stage search was therefore necessary. Most World Wide Web clients, including all versions of NCSA's Mosaic, support keyword searching of an HTML document once it is displayed in the viewing window. As it was out of scope for us to attempt modifying World Wide Web clients and servers, we accepted this limitation and concentrated on integrating a scheme for finding relevant documents, relying on the World Wide Web client to locate text of interest once the document was selected and opened.

Legend

■ Biography ● Staff ▲ Collaborative Efforts ★ Collaboratory Proposed

EMSL ***Research Interests***	***Tank Waste Remediation***	***Contaminated Soils and Groundwater***	***Health and Environmental Effects***	***Advanced Characterization***
• Characterization and Redesign of Biodegradative Enzymes	■●▲	■● ★		
• DNA/Cell/Tissue Damage from Radiation/Chemical Exposure			■●	★
• Catalytic Destruction/Conversion of Chemical Wastes		■●▲★		
• Design of Separations Materials for Removal of Radionuclides and Other Species	■●▲★			
• Molecular Level Understanding of Radiation-InducedChemistry			■●	■● ★
• Characterization of the Molecular Processes Involved in the Degradation of Waste Forms	● ★	●		
• Structure and Dynamics of Complex Fluids and Solutions	■●▲			
• Molecular Processes at Aqueous-Mineral Interfaces		■●▲★		
• Characterization of Heterogeneous Molecular Processes in theAtmosphere		● ★		
• Rational Sensor Design	■●▲★			
• Ultrasensitive and Specific Detection of Contaminants				■●▲★
• National Collaboratory for Environmental and Molecular ScienceResearch	■●▲★	■●▲★	■●▲★	■●▲★
• Advanced Computing for Environmental and Molecular ScienceApplications	■● ★	●		

Figure 2. EMSL Research Interests

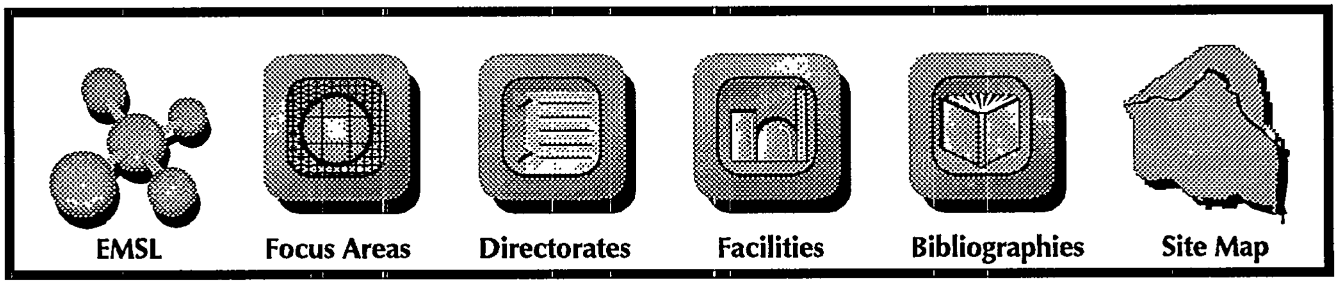


Figure 3. Standard EMSL Navigation Pallette

After an initial review of available schemes for searching World Wide Web information spaces was conducted, Wide Area Information Service (WAIS) was selected as the document level keyword search tool. WAIS was initially developed by Apple Computer, Thinking Machines, Dow Jones, and KPMG Peat Marwick, and is currently supported (now termed freeWAIS) by CNIDR (Clearinghouse for Networked Information Discovery and Retrieval). The product used to index the EMSL Information Space is KidofWAIS. KidofWAIS is a robust set of PERL scripts which INDEX the contents of UNIX directories. HTML may be the primary component of these information spaces, but KidofWAIS and other back-end WAIS systems can index other types of text documents (Microsoft RTF, Adobe Postscript, and PDF [Portable Document Format], for instance) and the titles of binary documents, such as JPEG and GIFs. During the initial setup of the WAIS indices, a quirk prevented operation of the search gateway. We learned that KidofWAIS limits the name of any particular index to a single word. This name is used by KidofWAIS to build a list of corollary files. Spaces and other nonstandard characters can be problematic. KidofWAIS will allow certain documents or directories to be ignored, based on file name. We modified one particular procedure that was in place for merging the EMSL private HTML files with their public components, by renaming the HTML files containing the private data to be merged to "*.priv." We were then able to instruct the indexing program to ignore files ending in ".priv," thus these files, which contain duplicate information and no formal HTML title, would not produce duplicate references and error messages. The EMSL private page was then modified to include both an ISINDEX anchor and a reference to the PERL script (some systems do not yet support ISINDEX manipulation, specifically the action= specification). These interface components can now be used to search the entire contents of the EMSL private information space by key word. Indexing of this information currently takes about 20 minutes on a Sparc 1+. Once a procedure has been completed, the indexing process can be submitted to one of the supporting systems by a CRON task.

Searching is required in both the WAIS space to list the documents with keyword matches, and then again in the document to find the particular term in the context of the World Wide Web page. We should strongly consider modifying the WEB server daemon to jump to the first match in the WEB document. EMSL staff and their collaborators on the World Wide Web will be able to search by keyword any document published in the EMSL information space. Private information is already indexed, and roll-out to public information space is expected soon.

Document Conversion to HTML

Although many types of formatted documents can be accessed through World Wide Web clients by launching helper applications, the platform-unique formats employed to generate professional reports, papers, and high-quality figures, images, and graphics make it impossible to guarantee that any information space browser will be able to make effective use of every document. Therefore, we focused on selecting and enhancing a few tools to convert from common word processing formats in use within EMSL to the HTML format. We focused on MicroSoft WORD, WordPerfect, LaTeX, and plain text.

For MicroSoft WORD and WordPerfect, we located and implemented a tool (RTFtoHTML) that does an excellent job of translating these documents to HTML. Documentation of the steps required was key because a multistep process is required. It is necessary to save a rich text format (RTF) version of the document initially, from within the word processing application. The RTFtoHTML application (for Macintosh - freeware) then translates the RTF document into HTML. We had planned to develop an additional tool that would generate hyperactive table of contents entries for such documents, but the need was obviated when a new RTFtoHTML version (2.7.4 - September 1994) was released during this project that provided this additional useful feature. We experimented with this feature sufficiently to discover that it was robust in its ability to recognize headings and turn them into appropriate table of contents entries. We recommend further investigation into this area, having a concern that some style management or style conversion guidelines may need to be established to ensure "pretty" HTML documents are produced from WORD and WordPerfect documents. Embedded graphics are also converted.

Similarly, for LaTeX documents, an excellent freeware conversion tool (latex2html) was located and implemented. The project documentation provided on the private EMSL World Wide Web pages includes instructions and documentation for employing this tool. Embedded graphics are also converted.

In order to provide some mechanism for converting a raw text document to a pseudo-latex conversion tool, tolatex, was developed. This tool evolved from an exercise in converting a document provided by Jarek Nieplocha (MSRC). This document describes a library (Global Arrays) for writing shared-memory parallel programs. One feature of the document is that it provides a list of definitions of library routines in one section and a list of prototypes in another section. Using the tolatex tool, it is relatively straightforward to provide hyperlinks between these two sections. In addition, one can insert other pseudo-LaTeX (as well as actual LaTeX) commands into the document and these will be converted into (hyper)LaTeX commands for the 'latex2html' conversion tool. See the README file (via World Wide Web) for usage of the 'tolatex' and 'totext' tools. Currently these tools are simple C programs that read from stdin and write to stdout. It may not be necessary to provide much further development of these tools, since if a document requires more formatting than is already provided, one should have used a word processing tool to begin with.

With the freeware tools selected, additional tools developed, and instructions and procedures provided, we have shown that common formats of documents produced within EMSL can be readily converted by users and by support personnel - into faithful reproductions in format.

Ethical, Legal, and Social Implications of the Human Genome Project for Screening, Monitoring, and Health Surveillance of Department of Energy Workers

Lowell E. Sever (Health Risk Assessment)

Project Description

The objective of this study was to examine a number of the implications of the Human Genome Project for genetic screening of Department of Energy workers. This was done by 1) reviewing relevant literature in genetics, ethics, law, and social policy; 2) holding discussions with experts from relevant disciplines; and 3) developing a white paper describing key issues. The white paper provided the basis for additional activities related to policies and options regarding application of methods from the Human Genome Project to DOE workers.

Technical Accomplishments

The accomplishments to date include the development of bibliographies relevant to technical and legal and ethical aspects of worker health protection and genetic screening and monitoring programs. Extensive references have been obtained, reviewed, and abstracted. Literature regarding exclusionary policies and legal implications of fetal protection policies has been reviewed as a possible paradigm for genetic screening policies related to genetic sensitivity to work-place exposure. Particular attention has been paid to literature on discrimination and privacy and legal and ethical aspects of genetic screening programs. A white paper has been developed which provided background for a proposal to the DOE Human Genome Project.

Discussions were held with experts in the areas of genetics and bioethics to explore some of the issues involved in worker genetic screening. This included participating in a DOE workshop on the use of biomarkers in worker health surveillance and a DOE conference on medical information and right to privacy. In addition, discussions were held with PNL staff to identify issues with particular relevance to programs directed by the DOE.

An outline for a workshop regarding the application of screening for genetic susceptibility to work-place exposures, growing out of the Human Genome Project, was drafted. The workshop is proposed to consider aspects of the Human Genome Project relevant to concerns about privacy and discrimination and related paradigms.

Hypermedia-Based Training

Frank L. Greitzer, William W. Brown, and Mary D. Zalesny (National Security and Defense—TPAC)

Project Description

Multimedia and hypertext technologies present an opportunity to enhance the quality and effectiveness of training, but there is a question about what exactly is learned in interactive multimedia training due to the potential lack of control over the student's progress through the material. The purpose of this project was to investigate innovative applications of user support functions that provide additional structure or guidance in accessing the training material. The research yielded a framework for assisting the instructor or course designer in tailoring the presentation to diverse training objectives.

With rapid advancements and declining costs of multimedia and hypertext technologies, an opportunity exists to enhance the quality and effectiveness of training. However, while these new forms of human-computer communication have been observed to be highly motivating for the user, their acceptance in the training field has not been overwhelming. The source of hypertext's great appeal is also its most troublesome barrier to acceptance by instructional designers. The high degree of interactivity provided through hypermedia shifts control over the sequencing and time of presentation to the student. The inherent lack of structure and potentially unlimited ability of the user to follow associative links may cause some users to feel "lost in hyperspace." Thus, students lose their location while exploring the learning material and move into areas that exceed their current understanding. For these reasons, some instructional designers lack confidence in what exactly is being learned in interactive multimedia training.

To improve the training experience, in terms of both motivation and learning, a more structured form of hypermedia-based training may be needed. The purpose of this project was to advance the state of the art of the emerging hypermedia technology through innovative applications of user support functions that provide additional structure or guidance in accessing the training material.

Technical Accomplishments

This project defined, explored, and evaluated innovative approaches to hypermedia-based training that are designed to facilitate the student's initial exposure to the material, as well as to enhance the review, remediation, or clarification of instructional materials.

The approach consisted of developing a framework for assisting an instructor or course designer to tailor the presentation of the material to diverse training objectives, student backgrounds, or scenarios. The major concepts addressed were

- Tailorable Course Design - The facility to adapt the material presented and paths through the material to varying training objectives and conditions.
- Student Guidance - A support concept that adds some structure to the user interface and serves as a filter or guide to direct the student's navigation through the material.

To illustrate the concepts, a prototype system was developed based on some existing computer-based training course material in the area of human factors.

Instructional Design Support

To implement the concepts of tailorable computer-based training and student guides, a more thorough specification of course content and objectives is required than in conventional course development. Therefore, a tool was developed to assist the designer/instructor with course definition and design. The tool, which mimics the process of course development, takes as input an outline of the topics of the course and enables the designer to customize the material on the basis of depth of coverage, context-sensitivity to student specialties, specification of topic prerequisites, and links to related material. The tool automatically generates a computer-based training shell upon which to build the training material.

Compared with the conventional linear computer-based training flow through the material, the course tailoring tool builds in flexibility to navigate through the material in a variety of ways, ranging from a fairly rigid linear sequence to more controlled browsing to unconstrained hypermedia navigation.

Electronic Teaching Assistant

This task explored and defined concepts for an electronic teaching assistant. An electronic teaching assistant is an agent that may help the student stay on track, inform the student about related topics, and support the tailoring of the content to varying objectives. For example, a guide may assist students who are less able to focus on problem areas or use the hypermedia system to its fullest potential. Guides also may be used to review specific content areas identified by the designer.

The electronic teaching assistant may perform such functions as periodically "checking in" with the student to see if work is progressing satisfactorily, support for modifying some of the tailorable features of the system (e.g., hypermedia access to related material), and help with navigation.

The electronic teaching assistant concepts were incorporated into the prototype on a conceptual, illustrative level. Implementation of the concepts will require additional research.

Interactive Prototype

The interactive prototype runs in MS-Windows on a 486-class personal computer. The system demonstrates the functionality of the instructional design support tool, the automatic generation of the computer-based training shell, and the concept of the electronic teaching assistant.

Conclusion

This research demonstrated concepts of interactive, flexible, and tailorable multimedia-based computer-based training systems. The prototype demonstrates the concept of adaptive computer-based training system design that will be necessary to meet the needs of modern training applications.

International Reactor Safety

Sam L. McKay (Safety and Performance Analysis)
Darrell F. Newman (Systems Engineering and Project Management)

Project Description

The objectives of this project were to continue to build on the development of PNL's insight and understanding of safety needs for the Soviet-designed commercial nuclear power reactors. This includes development and enhancement of those technical capabilities to address identified needs.

The focus of this activity continued to be directed at the graphite moderated, water cooled, pressure tube RBMK reactors, because it is in this type reactor that Hanford can offer unique capabilities and experience.

Technical Accomplishments

RBMK Tube Rupture Propagation Assessment

A significant area of safety requiring further evaluation involved the potential for a multiple tube rupture event within a RBMK reactor. This event, if mechanistically possible, could have a devastating impact on the overall safety of the design. Multiple tube ruptures, if not limited would ultimately result in the pressurization of the reactor cavity, lifting the cavity cover and exposing the core to the environment.

The initiating event involves the rupture of a reactor coolant system supply manifold (Group Distribution Header) and subsequent loss of coolant to its associated fuel channels. Eventually one or more of the impacted fuel channels will fail (burst) due to a loss of coolant-induced heating. Two safety issues arise with this failure.

1. The tube ruptures within the core cavity creating a local pressurization. Depending of the dynamic forces created by the initial failure of a fuel channel, adjacent channels could theoretically fail. An understanding of these forces is fundamental to the evaluation of the potential for this event. To quantify these forces, a more detailed investigation of the cavity pressurization and graphite stack fracture mechanics is required.

2. There exists a critical break size for the group distribution header that could result in flow stagnation to all 40+ tubes supplied by a given group distribution header. To address the potential for multiple tube rupture resulting from flow induced stagnation, it is necessary to characterize the failure times. In an attempt to define the most limiting conditions associated with this failure, tube failure times have been analytically evaluated with respect to power level, power distribution, and fuel channel flow.

These evaluations have been conducted with a RELAP5/MOD3 computer code specifically adapted by PNL for this application. These evaluations have shown that minimum tube failure times vary from 20 to 40 seconds for high power to average tubes, respectively. This is shown in Figures 1 and 2. This type of characterization will be coupled with future analysis of the group distribution header critical break size. This will allow a determination of the potential failure times to be made for different existing power distributions. The end result will be an estimate of the number of tubes that could be expected to fail before the flow stagnation is alleviated and adequate cooling is established.

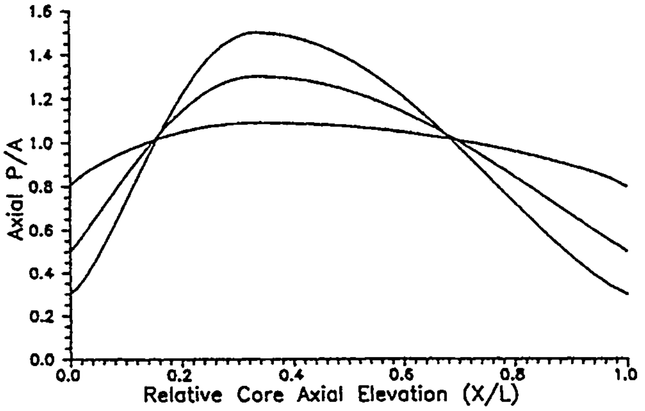


Figure 1. Bottom Skewed Axial Power Profile X/L=0.333 for P/A=1.10, 1.30, 1.50

Future investigations involving other mechanistically possible events resulting in multiple tube rupture scenarios will rely on this PNL-developed technology. These investigations are of significant international interest for the continued safe operation of the RBMK design.

RBMK Loss of Coolant Recovery Analysis

The ability to reestablish core cooling within a RBMK following a loss of coolant accident has been questioned. It is known that core flow oscillation and subsequent stagnation can occur within an RBMK core following a

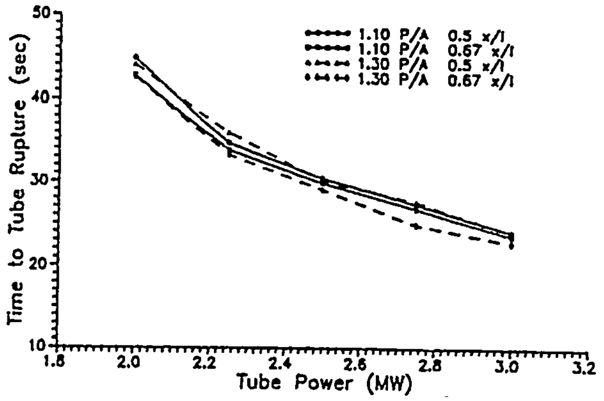


Figure 2. Tube Failure versus Tube Power (for different peaking)

loss of coolant accident or flow blockage in a group distribution header. This flow regime can challenge the ability of the normal cooling system or emergency coolant system to re-flood or establish core cooling. Fundamental to this understanding are the conditions which mark the entry into coolant flow instabilities (oscillations). Flow oscillations are subsequent to at least two phenomena known as flow density wave propagation and burnout-induced oscillation which have been successfully modeled and analyzed by PNL.

It was previously not known if RELAP5 could be effective in predicting flow instabilities for the RBMK. PNL studies have shown that flow instabilities in RBMK reactors appear to be dominated by burnout-induced oscillation. Investigation of density wave propagation potential has been inconclusive and is being investigated further.

Operational Insight

The understanding and improvement of operational safety for Soviet-designed commercial nuclear power reactors requires significant insight into many aspects of their design and operation. In pursuit of this understanding, PNL entered into a series of LDRD-funded activities that started with bringing three Russian scientists to the U.S. (PNL) under the SABIT program. The Russian scientists provided insight into reactor design, accident analysis, dose estimation, and waste management. This has led to development of a common understanding of the similarities and differences between the Eastern and Western technologies. Technology exchange to support the improvement of indigenous capabilities will ultimately contribute toward the promulgation of reactor safety for the Eastern designs.

These bi-lateral activities, involving the major Russian design institutes include:

- obtaining RBMK design specific and empirical information
- comparative analysis of codes and analytical methods
- assessment of Russian technical requirements for fuel cycle modifications
- determination of accident dose effects.

Conclusion

The project has been successful in demonstrating the complementary strengths of U.S. and Russian capabilities in addressing the operational safety issues facing the Soviet-designed facilities. The development of the technical and administrative infrastructure of countries which operate these facilities will ultimately result in effective solutions to these problems. PNL has gained significant insight into the problems and strengths of these owner countries and the applicability of U.S. technology in resolution of many of their safety concerns. This recognition has led to the selection of PNL as project manager for the DOE funded International Nuclear Safety Initiative.

Presentations

G. Tsiklauri. 1994. International Thermalhydraulics Conference, Pisa, Italy.

B. Schmidt. 1994. RELAP 5 Users Conference, Baltimore, Maryland.

Miniaturized Radiation Measurement Technology for Space Applications

Harry S. Miley (Chemical Sciences)

Project Description

A new technique for enhancing the sensitivity of small, portable detectors for field measurement of radioisotopes has been investigated and demonstrated. The key is that isotopes of interest in radioactive waste cleanup activities emit charged particles in coincidence with the gamma rays frequently used in analysis. In order to increase sensitivity to these isotopes, gamma rays from natural background isotopes (U-238, U-235, Th-238, K-40) are suppressed using an electronic identification scheme. This consists of a sheath of low-cost plastic scintillator surrounding the gamma-ray detector (Figure 1) and an appropriate electronic recording system.

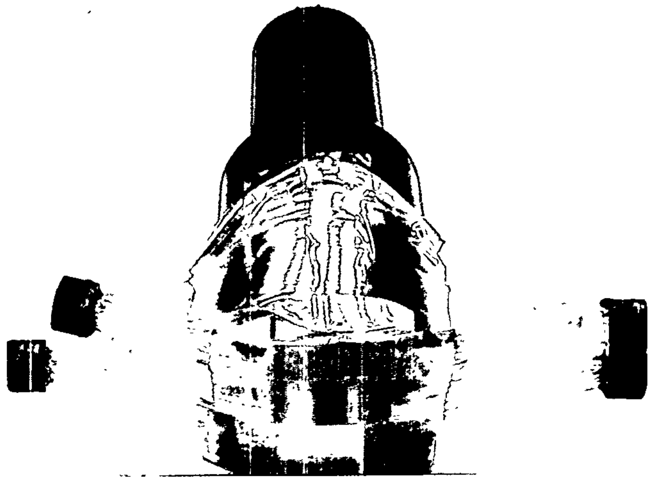


Figure 1. Sheath of Low-Cost Plastic Scintillator Surrounding the Gamma-Ray Detector

Technical Accomplishments

Although field gamma-ray measurements would most likely be carried out with a sodium iodide crystal (NaI), a germanium detector (Ge) was used for a laboratory mock up to allow much greater diagnostic capability. The germanium detector was protected from the laboratory radiation sources by a lead shield. Within the shield, radiation sources were located at various distances from the detector. A 1 mm sheet of charged particle detector was placed between the sources and the germanium. A series of coincidence circuits were constructed to allow simultaneous detection of beta particles and gamma-rays.

A marked reduction of non-local isotopes was observed in the data with a coincidence requirement compared to data without the requirement. For example, a remote (10 cm) K-40 source which has a 1460 keV gamma ray was drastically reduced (Figure 2).

In other words, by construction of this special detection system, radioisotopes in the immediate vicinity of the detector could be electronically separated from those more than a few millimeters away. This constitutes the aim of the project and it has been achieved.

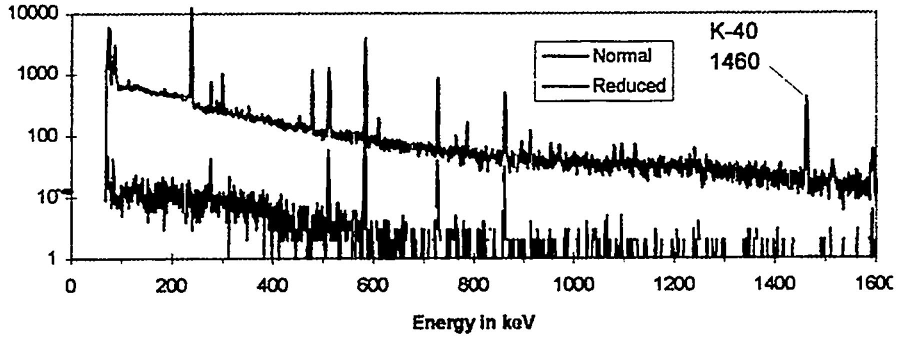


Figure 2. Coincidence Rejection

Nonlinear Optical Imaging

Robert J. Miller (Chemical Sciences)

Project Description

The objective of this research project was to explore the use of modern laser techniques to obtain three-dimensional images of molecular species concentrations within complex fluid and vapor flows, glasses, and other inhomogeneous media. This objective was pursued through a dynamic synthesis of fundamental phenomena by combining holographic and related detection methods with coherent optical techniques such as near-resonant Rayleigh scattering, resonantly enhanced Raman scattering, and four-wave mixing methods. Such imaging capabilities would provide the bases for advanced analytical technologies that are highly selective, ultrasensitive, and truly reliable for applications to environmental restoration and assessment activities.

Technical Accomplishments

Reclamation of any contaminated site requires the proper choices of methods of remediation. These choices must be based upon detailed knowledge of the contaminating species that are present and of the relative and absolute abundances of these contaminants. Evaluation of long-term waste storage strategies, such as vitrification, requires definition of the chemical and physical integrity of these storage media. Conservation and waste minimization efforts require monitoring of species in real time, directly within operating energy production and waste treatment processing facilities. Thus, both environmental restoration and assessment activities demand advanced analytical technologies that are highly selective, ultrasensitive, and truly reliable.

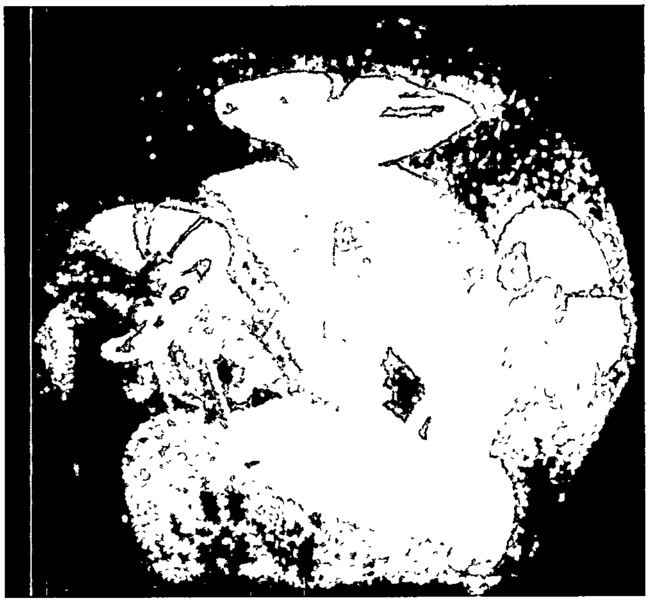
The availability of such analytical technologies applicable to the diverse materials produced by, and used during nuclear energy and weapons production cycles presents a formidable challenge. Vast quantities of organic chemicals, including carbon tetrachloride, acetone, and benzene, and a host of chelating agents, are either stored as mixed- and low-level wastes or have already leaked into the environment polluting large land areas and threatening ground- and surface-water supplies. Many of these chemicals are carcinogenic or highly toxic, and they pose a very real risk to human health and safety. Migration of radioactive and toxic heavy metals, and propagation of defects within vitrified wastes present equally formidable challenges.

Advances in modern laser techniques offer great potential for addressing the analytical needs of environmental characterization, monitoring, and assessment endeavors. This research project was, therefore, intended to develop and demonstrate noninvasive laser analytical technologies capable of providing three-dimensional images of environmental contaminants and energy-related waste materials in real time for field deployable, high sensitivity analytical applications.

During the past year, two experimental studies have been conducted in pursuit of the stated objective. The goal of the first study was to use near-resonant light scattering from cesium vapor to demonstrate construction of a molecular-species-specific hologram using high resolution, continuous-wave laser excitation. All experiments were performed on an effusive beam of cesium atoms under high vacuum to minimize interferences from Doppler-broadened resonance fluorescence and from collisionally induced fluorescence. Both the $6p_{1/2} \leftarrow 6s_{1/2}$ transition at 852.11 nm and the $7p_{3/2} \leftarrow 6s_{1/2}$ transition at 455.54 nm were probed as functions of experimental variables including laser excitation power and cesium beam density using various detection schemes and configurations. In no case was unambiguous evidence obtained for detection of a coherent, Rayleigh scattering process suitable for hologram formation. While the reasons for the apparent failure of these experiments remain unclear, it was deemed best to focus the limited resources of the project on the parallel study discussed below.

The aim of the second study was to determine well-defined limiting conditions for the successful generation of holographic images of various homogeneous and inhomogeneous, opaque and translucent media. This study was conducted in collaboration with the research group of Professor John Carlsten, Department of Physics, Montana State University.

There was particular interest in ascertaining the utility of laser light scattering with holographic detection for imaging of defects (e.g., small bubbles and cracks, within glasses). The photograph is of an holographic image of a simple, decorative glass paperweight. The tiny bubbles distributed throughout the bulk material are remarkably clear and the actual holographic image is far superior. This important result has profound implications for applications of three-dimensional holographic imaging to transparent or translucent vitrified wastes. The spatial distribution of even microscopic defects can be determined and their propagation through the bulk material can be monitored over time. By exploiting a resonant process, the concentration distributions of specific atomic, ionic, and molecular species imbedded within the material can be measured and their physical redistribution or chemical evolution can be monitored over time. The technology from this research project offers great potential for characterization of the physical integrity and chemical composition and transport of contaminants within vitrified waste materials.



Photograph of the virtual image from a transmission hologram of a glass paperweight. The small spots are tiny bubble defects distributed throughout the sample.

Probabilistic Finite Element Analysis

Mohammad A. Khaleel (Automation and Measurement Sciences)

Project Description

The objective of this project was to develop a probabilistic finite element code that can be used for accurate modeling of randomly varying fields in a finite element context. This work included development of an axisymmetric shell, an axisymmetric solid, a truss and beam element. Geometric nonlinearity was included using an updated Lagrangian approach. As required for probabilistic finite element analysis, derivative matrices were also developed and incorporated into a standard finite element program.

Structural failures generally occur under conditions of nonlinear and inelastic response. Therefore, the assessment of structural safety should be based on the inelastic and nonlinear behavior. The finite element method and continuum mechanics for the most part are developed and used in a strict deterministic context. These methodologies cannot accurately predict the response and safety of real structures which involve unavoidable uncertainties. Unfortunately, very little progress has been made to integrate the finite element method and structural reliability methods. As such, this computer program was focused on developing and implementing a comprehensive procedure for finite element reliability analysis of nonlinear and inelastic structures. Two existing computer codes CALREL (reliability code) and FEAP (finite element analysis code) are both extended and used to carry out probabilistic finite element analysis.

Technical Accomplishments

Our work resulted in the development of a probabilistic axisymmetric shell element including geometric and material nonlinearities using an updated Lagrangian approach. As required for probabilistic finite element analysis, derivative matrices were developed and incorporated into the FEAP code. Additional results of the analysis are the computation of the probability sensitivities. These sensitivities aim at measuring the rate of variation in the response of a structure with respect to the material parameters of the structure, its geometry, or applied loads. The sensitivity measures are expressed in terms of the derivatives of the response. These measures can be used in determination of relative importance of parameters, optimal allocation of resources, probabilistic analysis, and optimal structural design.

Several methods are available for computing the derivative of the structural response. The use of a finitedifference approach requires repeated solutions of the problem at least one time greater than the number of sensitivity measures. PNL staff used an alternative approach for computing response derivatives that was based on direct differentiation of the equations governing the response with respect to the variable of interest. Then governing derivative are assembled and solved according to standard finite element procedures.

An interface program was developed that links the CALREL and FEAP programs for discretization of random fields, allocation of arrays necessary for evaluation of derivative matrices, and automatic solution of the derivative responses through use of the macro programming language. For the analysis of complex structures, an interface code between the commercially available computer code ANSYS and the probabilistic finite element code was developed. The ANSYS code is mainly used to provide pre- and postprocessing of the input and output. This does not provide the level of flexibility and user friendliness necessary to make the current probabilistic finite element code commercially competitive.

Publications

M. A. Khaleel. 1994. "Reliability Analysis of Concrete Girders." *Proceedings of ISSAT International Conference on Reliability & Quality in Design*, Seattle, Washington, pp. 218-223.

M. A. Khaleel, W. F. Cofer, and B. K. Hatchell. "Stochastic Finite Element Analysis of Shell Structures, Part I: Theory." ASCE, *Journal of Structural Engineering* (to be submitted).

M. A. Khaleel, W. F. Cofer, and B. K. Hatchell. "Stochastic Finite Element Analysis of Shell Structures, Part II: Applications." ASCE, *Journal of Structural Engineering* (to be submitted).

Presentations

M. A. Khaleel. 1994. "Reliability Analysis of Concrete Girders." Presented at the ISSAT International Conference on Reliability & Quality in Design, Seattle, Washington.

M. A. Khaleel. 1994. "Probabilistic Finite Element Analysis." Invited lecture at the Department of Civil Engineering, Washington State University, Pullman, Washington.

M. A. Khaleel. 1994. "Application of Probabilistic Finite Element to Structural Safety of Hanford Waste Tanks." Presented at Westinghouse Hanford Company Tank Safety Committee. Richland, Washington.

M. A. Khaleel. 1994. "Application of Probabilistic Finite Element to Mitigation of Waste Turn-over at the Hanford Site." Presented to PNL Flammable Gas Program. Richland, Washington.

M. A. Khaleel. 1994. "Probabilistic Finite Element Analysis." LDRD Seminar, Richland, Washington.

Other Accomplishments

W. F. Cofe (Associate Professor of Civil Engineering) was hired from Washington State University, Pullman, Washington.

Properties of Soft X-Ray Absorption

Leslie A. Braby (Biology and Chemistry)

Project Description

Soft x-rays produced by a synchrotron light source provide a tool for evaluating the effects of clusters of radiation-induced chemical changes in biological systems. These x-ray induced clusters can be used to simulate the clusters produced by atomic processes along charged particle tracks. Current models of the biological effectiveness of ionizing radiation are based on the assumption that this clustered damage is more difficult to repair than isolated strand breaks in DNA, and that it is the difference in repair that is responsible for the increased effectiveness of radiations with high linear energy transfer (LET). It has proved to be difficult to test this assumption, partly because different radiations produce different mixtures of clustered and isolated chemical changes, but no conventional radiation produces only one or the other. However, the soft x-rays produced by synchrotron light sources, although difficult to work with, produce only clustered damage and the energy per cluster can be varied over a reasonable range. The goal of this project was to develop the techniques to use synchrotron x-rays to irradiate specific DNA structures and test the effectiveness of the resulting clustered damage in producing specific classes of damage.

In order to develop credible research proposals in the area of the effectiveness of clustered damage, two areas must be addressed: 1) an effective radiation source and exposure system which can deliver the required exposure in a few minutes, and 2) a biological system for assessing the amount and severity of damage which is precise enough to detect the expected small differences in irreparable damage in the large background of repairable damage. Since synchrotron light sources are available at only a few special facilities, and because beam time is somewhat limited, it is important to test the techniques with more conventional radiation sources before scheduling synchrotron time. The biological system can be tested initially using conventional x- or gamma-ray irradiation. A more realistic test of both the irradiation system and the biological assay can be obtained using proton and deuteron beams from the PNL tandem accelerator. These charged particle experiments will also provide data on the effectiveness of radiations with different, and calculable, degrees of clustering along the charged particle tracks.

Covalently closed circular double-stranded DNA of native plasmids serves as a good experimental model to examine clustering of damage in DNA. In addition to the amount of unchanged plasmid, single-strand breaks and double-strand breaks can be monitored following exposure to ionizing radiation. One single-strand break transforms the plasmid from the closed circular form to the nicked circular form, whereas a double-strand break, produced either directly or from random coincidence of single-strand breaks, transforms DNA from the closed circular or the nicked circular form to linear DNA molecules. All three forms of the plasmid are readily separated by agarose gel electrophoresis techniques.

In most previous experiments, detection of the different forms of the plasmid has been accomplished by intercalating ethidium bromide into the plasmid DNA following electrophoresis and then assessing conversion of the DNA into the different forms by observing the ethidium bromide fluorescence. Although this is a good qualitative technique, it is difficult to use it in a quantitative fashion because the degree of intercalation by ethidium bromide is different in supercoiled and linear DNA. This difference necessitated development of "correction" factors for each of the three bands produced in electrophoresis of irradiated plasmid DNA, and these correction factors introduced undesirable uncertainty in the experiments.

Technical Accomplishments

We have tested and refined an alternative approach for quantifying DNA which is based on commercially available bioreagents, termed the Genius System, designed for nonradioactive labeling in molecular biology studies. In general, the process utilizes a probe molecule constructed to complement a portion of the target DNA. The probe contains integrated digoxygenin-labeled deoxyuridine triphosphate and the amount of plasmid DNA is measured following a hybridization reaction. The digoxygenin-labeled probe bound to the plasmid DNA is then detected by antibody reactions specific for the label. An enzyme bound to antibodies is capable of reacting with a substrate termed Lumni-phos-530 to produce a chemiluminescent reaction which is recorded on photographic emulsion or by advanced spectroscopic detectors. The intensity of the chemiluminescence is directly proportional to the amount of DNA in each band in the gel and this can be used to measure the amount of different forms of DNA in the gel. Such information leads to analysis of the degree of double- and single-strand breaks in the plasmid DNA.

We originally used a plasmid, pGEM, which contains a T7 promotor site which allowed us to construct an RNA probe. However, preparation of large-scale quantities of this plasmid resulted in a family of topoisomers making this preparation unsuitable for examining DNA damage. Another plasmid, pBLUESCRIPT, was selected to avoid this problem. It consists of 2961 base pairs, and large quantities, purified from *E. coli* cultures, could be produced with >95% of the DNA in the supercoiled form and without significant contamination by topoisomers. An RNA probe was constructed by digesting the purified plasmid with ScaI (which cuts approximately 2000 bases from the T7 promotor site), permitting RNA polymerase-mediated incorporation of digoxygenin-dUTP. This probe was hybridized to samples of irradiated plasmid to measure strand breaks as a function of radiation dose.

We were able to further improve on this technique by using a DNA probe instead of the RNA probe. The DNA probe was constructed by randomly priming the plasmid with hexanucleotides and using the Klenow fragment of DNA polymerase to incorporate digoxygenin-labeled dUTP. This modification resulted in lowering of the background, higher stringency due to the ability to hybridize at higher temperatures, and, since hexanucleotides created random priming sites along the plasmid, the region for hybridization is generalized. This system was used to measure dose response curves for single- and double-strand breaks in the plasmid exposed to gamma radiation both in dilute solution and solutions with radical scavenging capacity equivalent to that in normal cells.

In order to be able to conduct parallel experiments using the synchrotron cell irradiation system developed at the University of Wisconsin and the charged particle irradiation system on the PNL tandem accelerator, it was necessary to develop a new sample holder. The primary characteristic of the holder must be that it maintain a very thin sample, only a few μm thick, to avoid excessive attenuation of the soft x-rays. A system which sandwiches the sample between a 1.5 μm thick plastic foil and a hydrophobic plastic plug was developed. This sample holder was designed to replace the petri dishes used in the Wisconsin system, and the PNL beam line was modified to accept the same type of holder. For charged particle irradiation, it is also necessary to measure the dose in the very thin sample in order to compare the effects of different radiations. This is best done using an extrapolation ion chamber, where the exact volume of the chamber can be determined from the slope of the ion current as the ion chamber plate spacing is varied. However, the irradiation system design is incompatible with conventional extrapolation chambers, so a special chamber was designed and built. This chamber will be used to calibrate the ion irradiation system as soon as accelerator beam time is available, and the plasmid system described above will be tested using the positive ion irradiation.

Prototype a Collaborative Scientific Work Environment

Daniel R. Adams and Anne Schur (Information Systems and Engineering)
James D. Myers (Computing and Information Sciences)

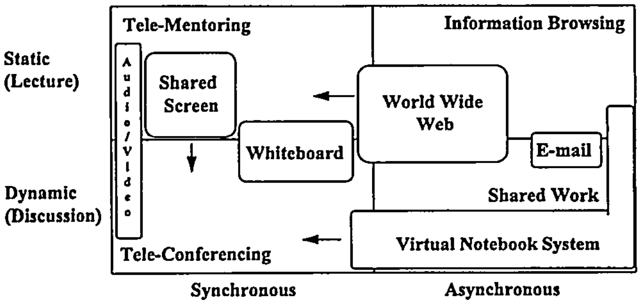
Project Description

The purpose of this project was to develop and evaluate a prototype of a system that enables computer-facilitated collaborations to take place between geographically dispersed scientists. In order to obtain real-world feedback, this prototype focused on facilitating collaboration between two non-collocated researchers working on nuclear magnetic resonance experiments. The prototype provided a collaborative work environment that enabled audio communications and interactive sharing of common workspaces, notebooks, and data by integrating public domain and commercial software products into a functioning collaborative environment. The prototype was used and tested at PNL. The experience gained, as well as the technological and social data gathered during the testing, helped lay the foundation for a larger effort over the next several years to develop a true "collaboratory."

Technical Accomplishments

Collaborations are critical to the advancement of the state of the art in all scientific fields. Traditionally, these collaborations have relied on face-to-face meetings and travel. However, networking and computer technologies have advanced to the point that it is reasonable to propose computer-facilitated collaborations between geographically dispersed scientists. Collaborative software environments can address several different modes of collaboration and the components required in the collaborative software environments vary accordingly (see the figure).

This research work focused on scientists working with nuclear magnetic resonance in a highly heterogenous computing environment. For example, Macintosh and other personal computers are found on desktops, SUN workstations are used to control the nuclear magnetic resonance experiments and data acquisition, and Silicon Graphics machines are used for data analysis and visualization. Thus, a collaborative software environment that facilitates remote collaborations in this domain must operate on, and across, all of these platforms. This goal was partially met.



Computer Support for Collaborations

We built a single collaborative software environment by integrating video teleconferencing, a shared notebook, a shared whiteboard with "cut and paste" capabilities, and a shared textual "chat" box. From experiments with this system we learned that

- the video teleconferencing capability was not critical and often was used to transmit pictures of paper documents
- the shared whiteboard and notebook were critical components for focusing discussions and sharing ideas
- the shared "chat" box was not used for the types of collaboration studied
- a critical component that was missing was a screen replication utility that allowed a live screen on one machine to be viewed from another.

The lack of a screen replicator was the most difficult problem to address. Several tools were located that worked in homogeneous UNIX environments, but all attempts to extend these to heterogenous environments, particularly those including Macintosh hardware, failed.

To be effective in a scientific research environment, a collaborative software environment must satisfy several constraints. It must function in a heterogeneous hardware environment. It must provide a capability to broadcast copies of a window from one machine to one or more others. It must provide a shared workspace, such as an electronic whiteboard or virtual notebook, and must have a consistent, readily understood user interface in order to be accepted and employed effectively by noncomputer scientists.

Re-Engineering Business Processes

Larry O. Levine, Joseph C. Montgomery, and Monty L. Carson (National Security and Defense—TPAC)

Project Description

The objective of this project was to build an operational framework that could support DOE in wrestling with significant business process re-engineering efforts. This framework could then be used to identify tools and techniques that can successfully and cost-effectively support the entire re-engineering process. Because of the high failure rate of re-engineering efforts reported in the literature, a framework and specific tools and techniques are needed for process re-engineering to be conducted successfully and cost-effectively.

Technical Accomplishments

Literature in a number of fields, particularly public administration, change management, and business process re-engineering were reviewed to understand the unique requirements for re-engineering in the public sector.

The project developed an analytical framework based on J. Q. Wilson's (1989) typology of government agency types. This framework enables a change agent to examine the preferred approach (re-engineering, reinventing, total quality management, or other) to improve performance of a specific agency based on a number of criteria:

- the amount of improvement required
- the time available to make improvement
- the measurability of mission accomplishment
- the observability of worker accomplishment/quality
- the larger organizational and social context
- the leadership available to drive improvement.

Reference

J. Q. Wilson. 1989. "Bureaucracy: what government agencies do and why they do it." Basic Books, Inc., New York.

Presentation

J. C. Montgomery. "Reengineering, TQM, and Reinventing Government — When Each is Appropriate and How to Integrate for Maximum Effectiveness." Paper accepted for presentation at the 3rd International Symposium on Quality and Productivity Improvement in Government. Institute of Industrial Engineers. February 27-28, 1995, Vienna, Virginia.

Real Time Dosimetry for Therapeutic Radiation Delivery

Richard A. Craig (Automation and Measurement Sciences)
Mary Bliss, Paul L. Reeder, and Debra S. Sunberg (Chemical Sciences)

Project Description

The objective of this work was to demonstrate the feasibility of using DOE-developed radiation-detection technology to develop a radiation detector capable of providing real-time dosimetry for the delivery of therapeutic radiation.

There are numerous documented cases in which therapeutic radiation misdelivery has resulted in serious injury or death of the patient. Currently, dosimetry for therapeutic radiation lacks spatial resolution, precise location at the area under treatment, and timeliness. PNL has extensive expertise in the development of rugged, solid-state, real-time radiation detectors and associated electronics. The original intent of this year's effort was to demonstrate a large-area dosimeter applied either to neutron therapy or to x-ray/gamma-ray therapy. The dosimeter would give real-time information about the radiation flux incident on and leaving the patient.

Technical Accomplishments

The first of these dosimeters would apply PNL's neutron sensitive scintillating glass fibers and the electronic technology developed to apply these fibers; the second would apply the electronic technology with commercially available plastic scintillating fibers.

The first step in determining which of these two dosimeters should be demonstrated first was to talk with practitioners in the field. The result of these discussions was the realization that there is a pressing need for real-time dosimetry in all the radiation therapy areas but there was identified an immediate and pressing need for a real-time dosimeter in boron neutron capture therapy (BNCT).

In BNCT, the patient is administered a pharmaceutical containing ^{10}B. The intent is that the boron will concentrate at the tumor site. This boron isotope undergoes a (n,α) reaction. The α-particle deposits most of its energy in a single cell; if several of these interactions occur in a cancerous cell, the cell can be destroyed. BNCT is primarily conducted on brain tumors at this time because the blood/brain barrier helps to prevent the boron-containing pharmaceutical from entering the normal tissue; the cancerous tissue does not have this protection.

This year, an analysis of a conceptual model for an in situ, real-time dosimeter for BNCT was completed; the conceptual design of this dosimeter is shown in Figure 1. The dosimeter consists of a short section ($\sim$1 cm) of PNL neutron-sensitive fiber attached to a length of passive fiber (to carry the signal out of the radiation field and to a photon-counting system).

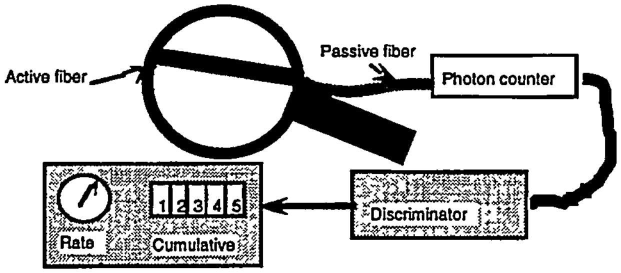


Figure 1. Conceptual Design for an In Situ, Real-Time Dosimeter for Boron Neutron Capture Therapy

The analysis showed that, for the neutron fluxes used in BNCT, signal rates could be on the order of 1 MHz. Pulse height for each neutron interaction observed was predicted to be on the order of 9 photoelectrons.

Most important, the detector would provide the information that could be used to determine the radiation dose in the vicinity of the detector. The reaction cross-section for the therapeutic ^{10}B interaction varies with neutron energy, as do other competing reactions that result in exposure to healthy tissue. The current thinking in the BNCT community is that the use of epithermal neutrons is more efficient than that of thermal neutrons simply on a basis of neutron economy. Epithermal neutron beams contain neutrons with a substantial range of velocities. It turns out that the cross section for interaction with the PNL sensor varies with velocity in the same way as that for the ^{10}B reaction and competing reactions. Thus, the sensor count rate is exactly proportional to the rates of these other reactions. Therefore, the count rate gives a measure of the real-time dose rate.

Some experiments on single fibers were also performed. Because the flux rates used in the laboratory are approximately six orders of magnitude smaller than those in BNCT, a coincidence technique was used to reduce the effects of photon-counter dark count. Figure 2 shows the results of this experiment for exposure to both a neutron field and beta-ray field. When adjusted for fiber parameters, the single-end pulse height (without a splice to a passive fiber) is approximately 12 photoelectrons.

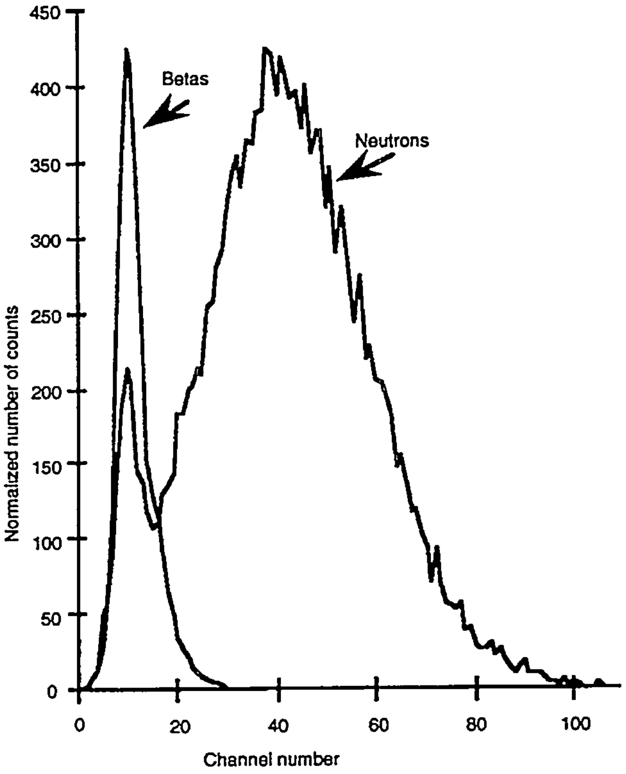


Figure 2. Pulse-Height Spectra (summed both ends) for Single Fiber Detector in Coincidence Arrangement

Publications

M. Bliss, R. A. Craig, P. L. Reeder, and D. S. Sunberg. 1994. "Development of a Real-Time Dosimeter for Therapeutic Neutron Radiation." To appear in the *Proceedings of the IEEE Nuclear Science Symposium.*

M. Bliss, R. A. Craig, P. L. Reeder, and D. S. Sunberg. 1994. "A Real-Time Dosimeter for Boron-Neutron Capture Radiation." *Proceedings of the Accelerator-Based Neutron Sources for Boron Neutron-Capture Therapy Workshop* (in press).

Presentations

M. Bliss, R. A. Craig, P. L. Reeder, and D. S. Sunberg. 1994. "Development of a Real-Time Dosimeter for Therapeutic Neutron Radiation." Accepted for the IEEE Nuclear Science Symposium, November.

M. Bliss, R. A. Craig, P. L. Reeder, and D. S. Sunberg. 1994. "A Real-Time Dosimeter for Boron-Neutron Capture Radiation." Presented at the Accelerator-Based Neutron Sources for Boron Neutron-Capture Therapy Workshop, Jackson, Wyoming. September 11-14.

Other Accomplishments

When fabricated, a prototype of this dosimeter will be used in clinical trials in collaboration with the Idaho National Engineering Laboratory team conducting this work.

Sonar Impulse Target Strength Holography

H. Dale Collins (Automation and Measurement Sciences)

Project Description

Previous work with the Navy (DTRC/Bremerton, Mr. Chuck Hinson) proved the viability of employing broad band holographic imaging techniques on full-scale submarines in Carr Inlet. The initial success of this passive signature program prompted continued work in this critical area.

This project consisted of using PNL's holographic imaging system, x-y scanner, and model nuclear submarine to generate high resolution images and target strength measurements. The proof-of-principle demonstration at scale frequencies provided experimental data to support a full-scale system in the future.

Sonar Impulse Target Strength Holography is a unique and efficient technique to acquire complex submarine acoustic scattering data in the near field. It has the efficacy to provide the Navy with extremely high resolution three-dimensional images of the reflected acoustic energy from submarines and reveal their "hot spots" at all sonar frequencies.

Technical Accomplishments

A small-scale model submarine (~2 m length) was imaged using scale millimeter wave frequencies of 100 to 112 GHz. This frequency range in air simulated acoustic frequencies (~4 to 6 KHz) in the ocean.

A multi-frequency image in three dimensions was made of a nuclear submarine with and without various simulated sonar absorbing materials on the hull. The images illustrated the resolution capabilities of the technique and clearly revealed the "hot spots" that tend to dominate the far-field target strength. The detectibility of our submarines is determined by their reflectivity at all threat frequencies and by the radiated energy from their hulls.

This near-field technique will provide a tool that has the capabilities to evaluate extremely low signature (stealth) submarines now and in the future.

Spectroscopic Holography

Kurt A. Stahl and Thomas Sloane (Automation and Measurement Sciences)

Project Description

The objective of this project was to develop the capability of performing three-dimensional, species-specific imaging of atoms or molecules with a characteristic absorption in the visible or infrared region of the spectrum. If successful, this technique will provide a method for three-dimensional spectroscopic imaging of the concentration of an atomic or molecular absorber in an otherwise non-absorbing medium.

Technical Accomplishments

Current capability in the three-dimensional spectroscopic imaging of chemical compounds is restricted to methods that require the time-dependent scanning of a point measurement technique or a planar imaging method. Although a holographic technique similar to the proposed method has been briefly investigated by at least two research groups, neither has yet demonstrated the ability to perform three-dimensional imaging. These researchers have used forward-scattered near-resonant radiation to obtain line-of-sight species concentration information from two or more views, followed by tomographic reconstruction to obtain three-dimensional information. This project concentrates on isotropically scattered nearresonant radiation which will allow three-dimensional information to be recorded in a single-exposure hologram.

The project was first funded in 1993. Cesium was selected as the test species due to the existence of an atomic cesium beam machine and high resolution lasers in a laboratory. Attempts were made to observe Rayleigh backscatter from the cesium beam using a continuous wave Ti:sapphire laser tuned to the strongest transition ($6s_{1/2}$-$6p_{1/2}$, in the near-infrared) of cesium. Ultimately, it was found that any potential backscatter would not be observed due to unwanted scattered excitation light in the cesium beam machine's vacuum chamber. However, relatively strong isotropic emission at and near resonance was observed.

In FY 1994, the project attempted to test for coherence in the observed emission. Due to difficulties in obtaining the use of the Ti:sapphire laser, the $6s_{1/2}$-$7p_{3/2}$ transition of cesium was pumped using a high resolution visible continuous wave dye laser. Attempts were made to form interference fringes between the emission and the excitation laser light in order to show coherence. No fringes were observed, but there were enough possible causes for the failure that a decision to continue was made. Contributors to the lack of success included a malfunctioning cesium oven, low optical intensity, high ambient light levels, and the potentially small contribution of Rayleigh light to the overall emission, which may well have been largely incoherent fluorescence.

During this round of experimentation, a very insightful technical paper entitled, "Collisional Redistribution and Saturation of Near-Resonance Scattered Light," by Carlsten et al. was obtained. The paper detailed the existence of several peaks in the optical emission from near resonance excitation. These peaks arise from Rayleigh scattering, three-photon processes, and fluorescence. Since only the Rayleigh scattering is usable for formation of a hologram, it was apparent that very careful filtering of the emission would be necessary. Telephone conversations with Carlsten indicated that the magnitude of the Rayleigh scattered light is typically a factor of around 4 lower than the fluorescence, so the fact that the combined emission was easily observed by eye indicates that there is hope of isolating enough Rayleigh light to form a hologram.

The monochromator, photomultiplier tube and housing, beam steering optics, mounting hardware and platform, ambient light shielding and baffling, etc., were collected, fabricated, and assembled as necessary to spectrally disperse the emission into its various components.

Testing of Noise and ELF Instruments for RF/MW Interference

Matthew H. Smith (Health Protection)

Project Description

Industrial hygiene instruments are used to assess health hazards in the work place. In many cases, they are used in environments that can interfere with their operation. Environmental exposure to radio frequency and microwave (RF/MW) fields has been shown in our study to interfere with the operation of noise dosimeters and instruments used to measure extremely low frequency magnetic fields.

Instruments were tested in accordance with American National Standard: Performance Specifications for Health Physics Instrumentation (ANSI N42.17A-1989). The results of this work could lead to specific recommendations for testing different types of industrial hygiene instruments.

Technical Accomplishments

During FY 1994 several types of instruments were tested for susceptibility to RF/MW fields. These instruments included a noise dosimeter (Instrument A), an extremely low frequency meter using an induction coil (Instrument B), and an extremely low frequency meter using a three-axis hall effect probe (Instrument C).

The instruments were tested for microwave susceptibility by exposing them at a power density of 10 $\mathrm{mW/cm^2}$ (frequency = 2450 MHz). Radio-frequency susceptibility was tested in the frequency range 0.3 MHz to 35 MHz. The field strength in this range was held at 100 V/m.

Instruments A, B, and C were all found to be susceptible (i.e., exposure reading differed by greater than 15% when compared to reference reading) to microwave exposure. Figure 1 illustrates the response of the noise dosimeter to microwave exposure. Instruments B and C were also susceptible to radiofrequency exposure. The results of these tests are shown in Figure 2.

Instrument C also demonstrated an lack of selectivity regarding fields it was designed to measure (both alternating current and direct current magnetic fields). When set up to measure static (direct current) magnetic fields it was found that adding exposure from an alternating current magnetic field source would alter the instrument's reading. The same problem occurred when measuring alternating current fields and an interfering direct current field was added. Instrument B was designed to measure alternating current fields exclusively. No susceptibility from interfering direct current fields was found.

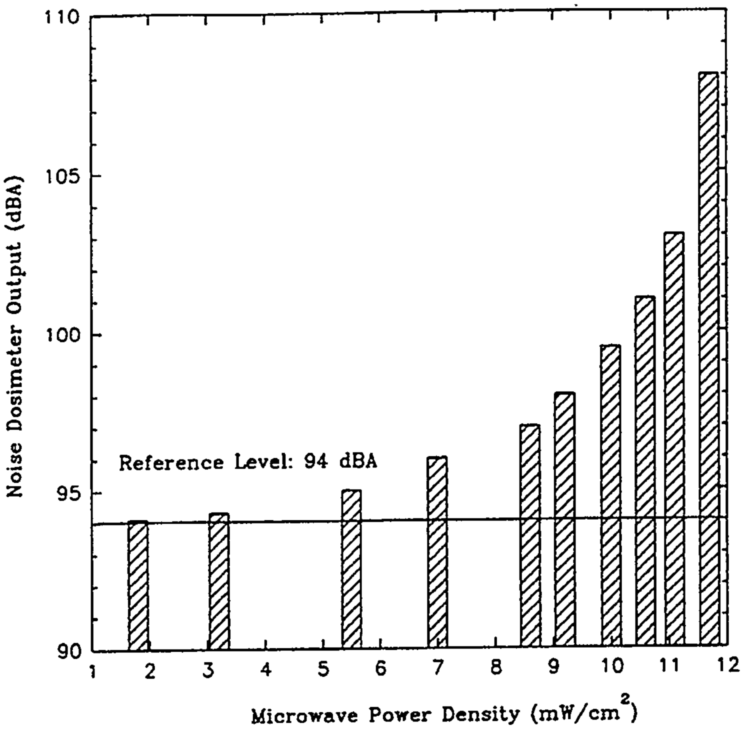


Figure 1. Response of Noise Dosimeter when Exposed to Microwave Field

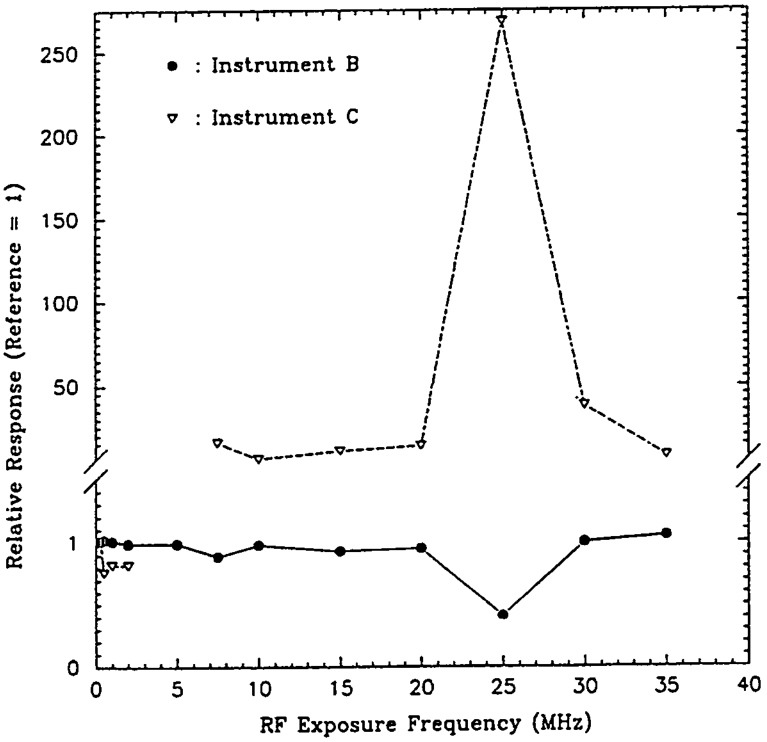


Figure 2. Relative Response of Instruments B and C to Radio Frequency Exposure

Ultrasonic Measurement of Elastic Properties of Bone

Gerald J. Posakony (Applied Physics)
Robert V. Harris and Angela Macedo (Automation and Measurement)

Project Description

Reduction of bone mineral content is characteristic of conditions such as osteoporosis, and can lead to a variety of compressional fractures such as those that occur in the neck of the femur. The accepted method for determining reduction in mineral content is radiography. This ionizing radiation procedure tends to be relatively expensive and the results qualitative. The objective of this proof-of-concept study is to evaluate ultrasonic attenuation and backscatter phenomena as an in vivo means for quantifying the degree of demineralization in bone. Ultrasonic technology offers the potential for a simple low-cost, noninvasive method for comparative determination of properties of bone.

Technical Accomplishments

Skeletal bones are very complex and their internal structure varies along their length. In bones such as the femur, the shaft is annular, hollow, and contains the bone marrow. In the body or shaft of the femur and other major bones, the cortex, or cortical bone, is a thick hard structure designed to carry heavy loads. Toward the joints the bone changes to a cellular, or cancellous structure. Changes in mineral content associated with osteoporosis initially appear in the cancellous structure and only at advanced stages does thinning occur in the cortical bone. Therefore the major interest in this project has been directed to the study of characteristics of ultrasonic wave propagation through cancellous bone structures.

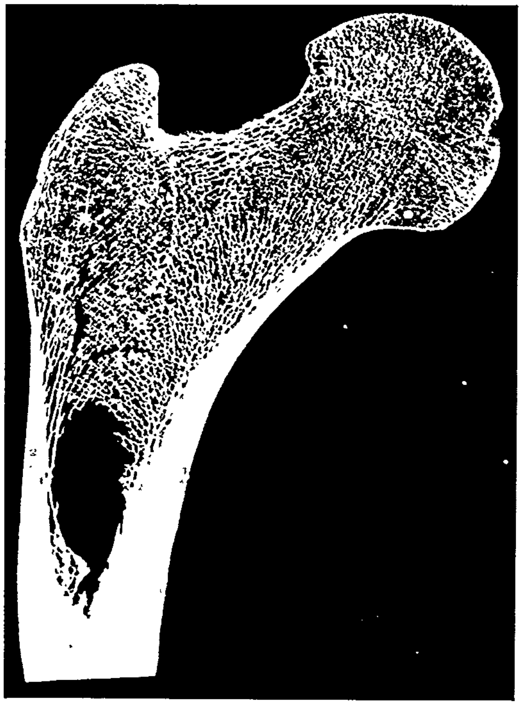


Figure 1. Photograph of the Cancellous Structure of the Head of the Femur

Figure 1 shows the cancellous nature of the head and neck of a femur where many hip fractures occur. The interior of the bone is very porous and covered by a thin cortex. Logically, ultrasonic waves propagating through the cancellous structure would be influenced by fluids in these cells and by their size and distribution. Ultrasonic waves passing through the cancellous structure should be attenuated by the structure and this attenuation should be dependent on the frequency of the ultrasound. Measuring the attenuation as a function of frequency should give a quantifiable indication of the nature of the structure.

The literature search carried out at the onset of the program produced many papers on ultrasonic measurement of the elastic properties of cortical bone. Ultrasonic velocity measurements show a correlation with the elastic properties obtained from mechanical tensile and shear tests. However, only a few papers discussed measurement of cancellous bone structure and the initial search located only one paper that contained sufficient detail to interpret the procedure followed. Studies have been made of the knee bone in marathon runners and with sedentary individuals showing that differences were present, but the results were very sketchy and only suggested trends. One paper (Langton, Palmer and Porter, MEP, Ltd. 1984) chose the heel (calcaneus) bone for measurement as it is readily accessible, has a relatively large volume, and its structure is nearly all cancellous in nature. Clinical studies on 60 women showed a relationship between age; postmenopausal women who had and those who had not suffered fracture of the head of the femur. Based on information gained from this article, the PNL project concentrated on studies of attenuation in the calcaneus.

Experimental Studies

Since the studies of bone, both in vivo and in vitro, can probably only be made through comparative measurements, the first task was to develop or obtain a synthetic reference that could be used as a control. Several different approaches were evaluated such as glass, ceramic, and plastic spheres in a closed container and attenuation in solids. These proved to be unsatisfactory as they lacked reproducibility. Ceramic filters of the type used in filtering metal during the casting of parts proved to be a very good control material. These materials are very porous and are available with different pore sizes. The attenuation and frequency response were similar to the range of data given by Langton et al. in the 1984 paper.

The laboratory system used for these studies included a Wavetek Model 95 tone-burst generator, a broadband amplifier, and a Tektronix Model 2252 recording oscilloscope. Special transmitting transducers were fabricated that were designed to operate at the specific frequencies of 140, 320, 610, and 1000 kHz. This range was chosen based on information obtained from various articles. To ensure the phase fidelity of the ultrasonic wave propagating through the complex cancellous structure, a broadband, point-source transducer was selected as the receiver. The maximum voltage applied to the transmitting transducer during these studies was a 6-cycle, 15-volt pulse set for the specific frequency.

Initially, efforts were made to use bovine and sheep bones for experimentation. Attempting to propagate ultrasound through cancellous structure in these bones proved impractical. There was simply too much variability in the measurements and the fluids in the cancellous cells were unstable. A decision was reached to use calcaneus bones from cadavers and a number of bones were purchased from Ward's Natural Science of Rochester, New York. Nine bones were used in the experiment. Prior to making any measurements, the bones were weighed and their thickness measured. Then the bones were immersed in water, placed in a vacuum and degassed at rough pump pressures. To ensure that all air was removed, the process was repeated.

The results of ultrasonic measurements are shown in Figure 2. This is a plot of ultrasonic attenuation versus the frequency of wave propagation. The data were calculated from the amplitude of the waveform recorded on the printout of the oscilloscope record. All data were normalized for thickness of the bone. At 140 kHz there was little difference in attenuation. At 310 kHz differences of a few decibels (dB) were noted and this difference increased as the frequency was raised. At 1000 kHz differences as great as 20 dB were recorded.

Further, it was possible to separate the nine heel bones into three qualitative zones, namely low, medium, and high attenuation. Three of the bones fell into each category. There was no correlation between weight of the bone and attenuation. The dashed line is the attenuation response of the control specimen.

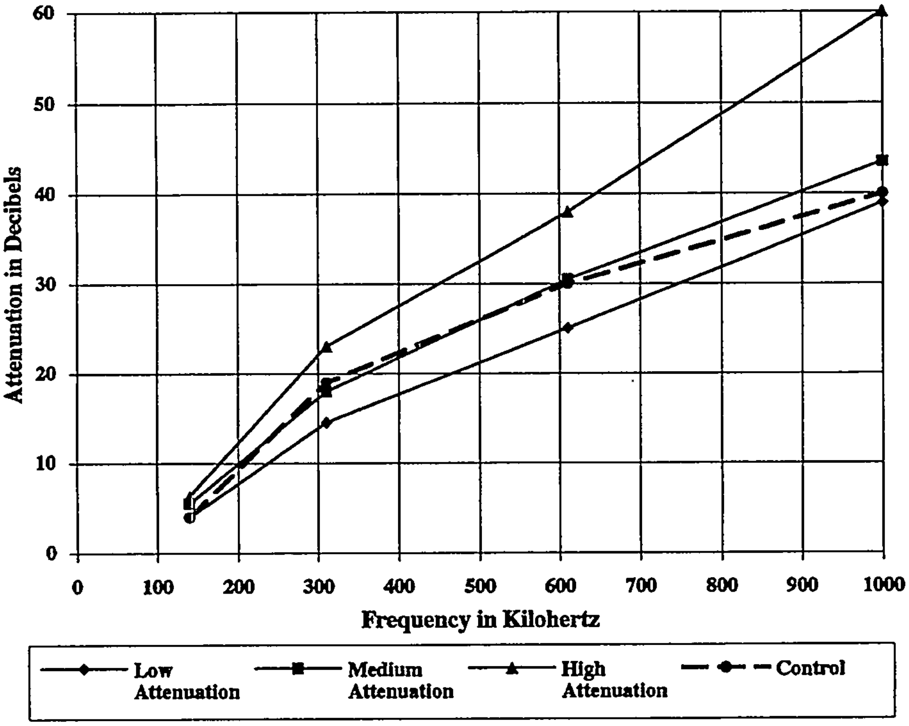


Figure 2. Results of Ultrasonic Attenuation Studies of the Calcaneus

At 1000 kHz the apparent separation (20 dB) should be sufficient to provide quantitative information; but with such a small population, only a proof-of-concept can be established. Attempts were made to obtain both back and lateral scatter information from the cancellous structure. This proved to be unsuccessful. The acoustic noise in the water pan used for the experiment exceeded the signal from backscatter. Velocity differences between ultrasonic waves propagating through water and those propagating through the calcaneus were negligible, thus only attenuation data was recorded.

An attempt was made to reproduce the data from the Langton article using the same ultrasonic transducer and similar ultrasonic equipment. In the laboratory we were unable to achieve the lower frequency information described in the article.

The project was started in July 1994 and closed on September 1994. In September, following discussions with a professional associate, we were advised that a company called Walker Ultrasonics in Worchester, Massachusetts, was marketing an instrument called the Ultrasonic Bone Analyzer (UBA). Discussions were held with Mr. Phil Townsend, company president, to learn more about this instrument. The literature and information received indicated a similarity with the approach taken in the PNL study. However, the UBA is different in that it is a sweep frequency device that provides a value for the derivative of the slope of the attenuation curve over the range 200 kHz to 600 kHz. Clinical studies have been performed in Europe using this device and Mr. Townsend stated that clinical studies were presently on-going in Hawaii. PNL's work provided attenuation in decibels per centimeter, relating results to a physical phenomenon.

Conclusion

Ultrasonic attenuation of the cancellous structure of the calcaneus appears to provide a means for detecting the onset or presence of reduction in mineral content of the cancellous bone structure. Results of the PNL test indicate that at frequencies of 500 to 1000 kHz a quantifiable difference exists in the specimens tested. However, the sampling was too small and too limited to draw any conclusions other than that there are differences in unknown specimens. While the results are encouraging, further work to develop and validate a demonstration prototype and to perform controlled clinical studies would be required to extend the work beyond the present stage. The study shows that the approach has potential, but it is the opinion of the researchers that measurement frequencies in the 750 to 1000 kHz range are needed to obtain meaningful diagnostic data.

Video-Based Imaging Interferometry

Charles R. Batishko (Automation and Measurement Sciences)

Project Description

A variety of video-based imaging interferometric techniques have recently received increased attention in the literature. These techniques make use of coherent light so as to result in interference among multiple video frames, or between a stored speckle field video image and a live speckle field video image. In addition, recent publications increasingly report success in making holograms through single-mode optical fibers. This project will attempt to develop the imaging interferometry techniques to the level of tools available for routine problem solving, then investigate the capability of implementation through fiber optics for nondestructive testing in inaccessible locations.

Technical Accomplishments

During FY 1993, this project investigated video holography. Funding was used to rewrite and debug code in an effort to improve the image acquisition and analysis algorithms. Hardware was assembled and samples manufactured to provide a test bed for the technology. By the end of FY 1993, images of a sample with a paper clip pattern imbedded in an epoxy substrate could be recognized in a noisy background.

The software was refined during FY 1994 so that current results were somewhat better than those achieved by the end of FY 1993. An example of a processed image of a PNL-shaped pattern made of paperclip wire, imbedded a few millimeters deep in epoxy, was prepared. While the image was still noisy, the pattern was readily detectable.

It is interesting to note that the stress applied to the sample which results in the generation of interference between a "before" and "after" condition is applied by illuminating the sample with a flash of light from a photographic electronic flash unit. Absorption of light by the sample results in generation of a very small amount of heat, which diffuses through the sample and causes differential heating/expansion of the paperclip wire, and thus the stress in the sample.

Testing was not completed to the degree desired. No additional samples were tested to determine the range of sizes and materials that could be imaged.

The intent had been to develop a graphical user interface (GUI), but this was not accomplished due to the significant investment required in software development tools, and required recoding of drivers for the framegrabber to allow use of framegrabber library functions in the image processing algorithms. Instead, a DOS character-based interface was developed, which, while not as visually appealing, nevertheless provides a simple, prompted means of acquiring and processing data.

Since the breadboard for packaging the system was not delivered until nearly the end of the fiscal year, packaging could not be completed.

The result of this project was a prototype video-based holographic interferometry system which, for the limited samples presented to it, is capable of visually displaying the presence of an internal anomaly. The value in the project was to provide a working system available for future use, and a foundational level of expertise in video holographic nondestructive testing.

Weapons-Grade Plutonium Disposition

Sam L. McKay (Safety and Performance Analysis)
Darrell F. Newman (Systems Engineering and Project Management)

Project Description

The objectives of this project were to continue the development of an enhanced and insightful understanding of the disposition options for surplus weapons-grade plutonium, enhance the technical capabilities to address these options, and to interact technically with Russian scientists on the feasibility of concepts proposed for burning weapons-grade plutonium. The focus of these studies has been directed at exploring the feasibility for Russian light-water-cooled reactor technology (principally the RBMK) to use surplus plutonium as a fuel to denature the weapons-grade material to reactor grade.

Technical Accomplishments

Interest has increased with regard to the reactor options which are reasonable and politically feasible to allow for the disposition and elimination of weapons-grade plutonium within Russia. The consideration of plutonium as a fuel in the RBMK system requires a significant understanding of its impact on the operational and safety performance of the core. PNL has implemented a series of activities designed to provide a preliminary analysis of the potential of this disposition option. These activities include the following:

- review of applicable codes to perform mixed oxide fuel calculations for the RBMK design
- provide a burnup-dependent assessment of core neutronics of mixed oxide fuel based on the use of weapons-grade plutonium in the RBMK
- assess the impact of changes from the present core reactivity and void coefficient that would be obtained from the use of mixed oxide fuels
- provide an preliminary assessment of the adequacy of present RBMK analytical models for neutronic system performance prediction when applied to mixed oxide fuels containing plutonium
- assess the void fraction and critical heat flux margins for thermal hydraulic stability required for utilization of mixed oxide fuels containing weapons-grade plutonium
- estimate the ability of the RBMK power system to consume weapons-grade plutonium
- provide evaluation of the transient performance using joint numerical analysis of neutronics and thermal hydraulic characteristics of the RBMK power systems which utilize mixed oxide fuels containing plutonium
- describe initial concepts for plutonium burning in existing Russian production reactors.

The project has been successful in demonstrating the viability of several weapons-grade plutonium disposition options which are technically acceptable to the user countries. PNL has gained significant insight into the problems facing the disposition options and applicability of U.S. technology in their resolution. Our funded activities have provided the opportunity for U.S. experts to interact at the working level with Russian scientists. This interaction has led to the establishment of common approaches to the development of disposition options not previously recognized. Recognition of these working relationships, as well as those developed in the International Reactor Safety Initiative, has led to the selection of PNL as project manager for the DOE-funded International Nuclear Safety Initiative.

Other Accomplishments

This project in conjunction with the International Reactor Safety project, and the SABIT program has brought a senior Russian scientist to PNL to work on plutonium disposition options involving the Russian reactors.

Acronyms and Abbreviations

Acronyms and Abbreviations

3E	energy, economics, environmental
5-BrU	5-bromouracil
ALARA	as low as reasonably achievable
APS	Advanced Photon Source
AREST	Analytic Repository Source Term
ARM	Atmospheric Research Measurement
ATCC	American Type Culture Collection
AWU	Associated Western Universities
BNCT	boron neutron capture therapy
BPDE	benzo[a]pyrene diol epoxide
C23O	catechol-2,3-dioxygenase
CE	capillary electrophonesis
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CPMAS	cross-polarization magic-angle spinning
CRAMPS	Combined Rotation and Multiple-Pulse Spectroscopy
DNA	deoxyribonucleic acid
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DNAPL	dense nonaqueous phase liquid
DQCM	dual quartz crystal microbalances
DSTLF	distribution short-term load forecasting
EDTA	ethylenediaminetetraacetic acid
EMSL	Environmental Molecular Sciences Laboratory
EPA	U.S. Environmental Protection Agency
EPIC	erosion productivity import calculator
EPR	electron paramagnetic resonance
ER&D	Exploratory Research and Development
ESI	electrospray ionization
ESI-MS	electrospray ionization mass spectrometry
FLAPW	full potential linearized augmented plane ware
FTICR	Fourier transform ion cyclotron resonance
FTICR-MS	Fourier transform ion cyclotron resonance mass spectroscopy
GCAM	Global Change Assessment Model
GCTE	Global Change and Terrestrial Ecosystems
GCRP	Global Change Research Program
HPLC	high performance liquid chromatography
HTML	Hypertext Markup Language
LEED	low energy electron defraction
LMDS	locally, multiply damaged sites
LDRD	Laboratory Directed Research and Development
MELF	monitored endpoint load forecaster
MINK	Missouri, Iowa, Nebraska, and Kansas

NA3E	North American economic-energy-environmental
NAFTA	North American Free Trade Agreement
NAPL	nonaqueous phase liquids
NEPA	National Environmental Policy Act
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NOAA	National Oceanic and Atmospheric Administration
NRC	Nuclear Regulatory Commission
NSF	National Science Foundation
NSLS	National Synchrotron Light Source
NTA-Mo	nitrilotriacetate monooxygenase
OGCMs	ocean general circulation models
OLAM	optimal linear associative memory
PANi-Pd	polyaniline-palladium
PAH	polynuclear aromatic hydrocarbon
PASC	Pulse Amplitude Synthesis and Control
PCB	polychlorinated biphenyl
PBPK	physiologically based pharmacokinetic
PCNA	proliferating cell nuclear antigen
PG&E	Pacific Gas and Electric
PNC-CAT	Pacific Northwest Consortium Collaborative Access Team
PNL	Pacific Northwest Laboratory
PNL-RCM	PNL-Regional Climate Model
RCRA	Resource Conservation and Recovery Act
RF/MW	radio frequency/microwave
RTDS	Rapid Thermal Decomposition of precursors in Solution
SGFET	Suspended Gate Field Effect Transistor
SGM	Second Generation Model
SGSIM	Sequential Gaussian Simulation
SMCC	Subsurface Microbial Culture Collection
SPC/E	extended single point charge
SPMDs	semipermeable membrane devices
SPSH	six-phase soil heating
TCSC	thyristor controlled series capacitor
TEMPEST	Transient Energy Momentum and Pressure Equations Solutions
TRIC	time resolved ion correlation
TRUEX	transuranium extraction
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service
UV/VIS	ultraviolet/visible
WAIS	Wide Area Information Service
XAFS	x-ray absorption fine structure