Laboratory Directed Research and Development Annual Report

Fiscal Year 1992

January 1993

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

Pacific Northwest Laboratory
Richland, Washington 99352
## Contents

- Introduction ......................................................................................................................................... ix
- Overview and Management Process ...................................................................................................... xi
- 1.0 Laboratory-Level Projects
  - 1.1 Integrated Environmental Research
    - A Novel High Resolution, High Sensitivity Infrared Technique for the Detection and Analysis of Gas Phase Molecules and Clusters ......................................................... 1.1.1
    - Advanced Instrumentation for Materials and Interfaces .................................................................... 1.1.3
    - Advanced Separations and Mass Spectrometry ................................................................................... 1.1.4
    - Advanced Software for Molecular Science Computations ................................................................. 1.1.7
    - Background Aerosol Optical Depths From Astronomical Archives ...................................................... 1.1.9
    - Biodegradative Enzyme Design .......................................................................................................... 1.1.11
    - Carbon Protocol Analysis .................................................................................................................. 1.1.14
    - Chemical Adducts and Radiation Sensitivity of Supercoiled DNA .................................................... 1.1.15
    - Chemical Processes at Interfaces ....................................................................................................... 1.1.17
    - Chemical Sensors and Interphase Chemistry ...................................................................................... 1.1.18
    - Child Health and Welfare Index ........................................................................................................ 1.1.19
    - Computer Modeling of DNA Perturbations .......................................................................................... 1.1.20
    - Computing and Information Sciences Hardware .................................................................................. 1.1.21
    - Computing and Information Sciences Software .................................................................................. 1.1.22
    - Contaminant Risk Evaluation and Management ................................................................................... 1.1.23
    - Cytofluorimetric Applications for Identifying Altered Molecular Markers ........................................ 1.1.24
    - Development of Tunable Ultrafast Laser Sources for Studying Real-Time Chemical Dynamics .......... 1.1.25
    - Earth and Environmental Sciences Research Related to Global Change ........................................... 1.1.26
    - Ecological Modeling .......................................................................................................................... 1.1.29
    - Enzymatic Transformation of Inorganic Chemicals .............................................................................. 1.1.30
<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epidemiological Study to Examine the Relationship Between UV-B Induced</td>
<td>1.1.32</td>
</tr>
<tr>
<td>Immunosuppression and Infectious Diseases in Humans</td>
<td></td>
</tr>
<tr>
<td>Fundamental Research in Subsurface Environmental Science</td>
<td>1.1.33</td>
</tr>
<tr>
<td>Genetic Profiling of Subsurface Microorganisms</td>
<td>1.1.36</td>
</tr>
<tr>
<td>Global Environmental Decision Making</td>
<td>1.1.37</td>
</tr>
<tr>
<td>High Field NMR and NMR Imaging</td>
<td>1.1.39</td>
</tr>
<tr>
<td>High Performance Computing</td>
<td>1.1.40</td>
</tr>
<tr>
<td>Improved Radionuclide Characterization</td>
<td>1.1.41</td>
</tr>
<tr>
<td>Infrared Atmospheric Continuum Absorption</td>
<td>1.1.43</td>
</tr>
<tr>
<td>Integrated Regional Climate Change</td>
<td>1.1.46</td>
</tr>
<tr>
<td>Integration of Molecular Research with Environmental Phenomena</td>
<td>1.1.47</td>
</tr>
<tr>
<td>Kinetic EPR Spectroscopy to Resolve Sorption Mechanisms</td>
<td>1.1.48</td>
</tr>
<tr>
<td>Land Use and Agricultural Model of Global Environmental Change</td>
<td>1.1.50</td>
</tr>
<tr>
<td>Magnetic Resonance Spectroscopy</td>
<td>1.1.52</td>
</tr>
<tr>
<td>Materials Surface Chemistry</td>
<td>1.1.53</td>
</tr>
<tr>
<td>Materials Theory and Modeling</td>
<td>1.1.56</td>
</tr>
<tr>
<td>Mineral Physics and Chemistry Relationships</td>
<td>1.1.59</td>
</tr>
<tr>
<td>Molecular Dynamics at Solid Surface Interfaces</td>
<td>1.1.60</td>
</tr>
<tr>
<td>Molecular Mechanisms of Carcinogenesis</td>
<td>1.1.61</td>
</tr>
<tr>
<td>Molecular-Scale Investigations of Alkali Halides</td>
<td>1.1.63</td>
</tr>
<tr>
<td>Multicenter Hazardous and Radioactive Waste Treatment</td>
<td>1.1.64</td>
</tr>
<tr>
<td>Multivariate Adaptive Regression Spline (MARS) Approximation Methods</td>
<td>1.1.67</td>
</tr>
<tr>
<td>Naturally Occurring Metal Chelates: Structure/Stability Relationships</td>
<td>1.1.68</td>
</tr>
<tr>
<td>Probing of DNA in Environmental Microbial Populations</td>
<td>1.1.69</td>
</tr>
<tr>
<td>Radiation Induced DNA-Protein Cross-Links</td>
<td>1.1.70</td>
</tr>
<tr>
<td>Radiative Forcing by Anthropogenic Aerosols</td>
<td>1.1.72</td>
</tr>
<tr>
<td>Radiometry for Pacific Northwest Laboratory's Gulfstream G-1 Research Aircraft</td>
<td>1.1.73</td>
</tr>
</tbody>
</table>
Real-Time Studies of Chemical Reaction Dynamics in Molecular Cluster Ions .......................... 1.1.74
Redesign of Biodegradative Enzymes: Theory Development and Coupled Theory-Experiment Approach .......................................................... 1.1.76
Scale Averaging of Effective Parameters: Synthetic Multiscale Simulation System Design .......................................................... 1.1.79
Site Specific DNA Damage by Radiation and Chemicals ......................................................... 1.1.80
Solid Waste .................................................................................................................. 1.1.82
Spectroscopy Techniques for Analysis of DNA Damage .......................................................... 1.1.84
Structure/Function Studies of DNA Repair Processes ............................................................ 1.1.86
Synchrotron Research/Advanced Photon Source Beamline ..................................................... 1.1.87
Technological Response ........................................................................................................ 1.1.88
Terra Vision ...................................................................................................................... 1.1.90
Training Initiative for Managing Highly Hazardous Chemical Processes .................................. 1.1.91

1.2 Process Science and Engineering
Advanced Catalysts and Catalytic Processes ............................................................................. 1.2.1
Advanced Coatings ............................................................................................................... 1.2.2
Electronic Synthesis: Polymer Multilayer Thin Film Deposition ............................................. 1.2.4
Fluid Dynamics Research ...................................................................................................... 1.2.5
In Situ Monitoring of Ultra-Fine Particle to Particle Material Interactions ................................ 1.2.8
Materials Synthesis .............................................................................................................. 1.2.9
Process Engineering Science ................................................................................................. 1.2.10
Separation Chemistry ........................................................................................................... 1.2.12

1.3 Energy Distribution and Utilization
Application of AI Technology to Power Plant Operations and Maintenance .......................... 1.3.1
Chemical Process Efficiency .................................................................................................. 1.3.3
Development of Advanced Flow Cytometry Methods for Investigating EMF-Induced Calcium Ion Mobility ........................................................................ 1.3.4
Diagnostics and Controls ...................................................................................................... 1.3.5
Laser Energy Receivers .................................................. 1.3.7
Magnetic Shielding Materials ........................................... 1.3.8
Power System Dynamic Analysis ....................................... 1.3.9
Transportation Materials ................................................ 1.3.10
Ultralight Fabric Radiator Development ............................... 1.3.11
Visualization of Energy and Power Systems Data .................... 1.3.12

1.4 Other Lab-Level Projects

International Germanium Experiment .................................. 1.4.1
Vertical Integration of Science, Technology, and Applications (VISTA) .......... 1.4.3
Weapons-Grade Plutonium Denaturing ................................ 1.4.5

2.0 Center-Level Projects

2.1 Applied Physics

Application of Holographic Principles to Eddy Current Coil Impedance Data
to Enhance Defect Image Resolution .................................. 2.1.1
Applications of Real-Time Statistical Quality Assessment .............. 2.1.2
Automatic Test Generation ................................................. 2.1.4
Computational Modeling of Room Air Convection and Ventilation Effectiveness .......... 2.1.5
Energy End-Use Data Analysis Environment and Toolkit ................ 2.1.6
Ensemble Averaging of Multiphase Flow Equations ..................... 2.1.8
Geographic Visualization and Animation ................................ 2.1.9
Infrared Fiber Optic Hydrocarbon Vapor Sensor for DOE Environmental
Applications ....................................................................... 2.1.10
Low Thrust Trajectory Optimization ..................................... 2.1.11
Microtechnology for Energy Applications ............................... 2.1.12
Pen-Based Energy Building Software .................................... 2.1.13
Semantic Data Modeling for Scientific Data Exchange .................. 2.1.14
Sonar Impulse Target Strength Holography .............................. 2.1.15
2.2 Earth and Environmental Sciences

Advanced Wind Speed Sensor .................................................. 2.2.1
Developing a Framework for an Advanced Air Toxics Model ....................... 2.2.2
Extraction of Organic Contaminants by Supercritical Fluid Extraction ............... 2.2.3
Feasibility of Using Analog Processing for Geographically Integrating Hanford
Environmental Information for Technical and Nontechnical Uses ..................... 2.2.4
Modeling of In Situ Bio restoration of Organic Compounds in Groundwater Using
High Performance Computers ......................................................... 2.2.5
Quantum Geochemistry: Oxide Mineral Interfaces ..................................... 2.2.6

2.3 Life Sciences

Appliance Use and Cancer .................................................................. 2.3.1
Development of a Ribbon Channel Plate for DNA Sequencing ....................... 2.3.2
Development of Direct Skin Beta Dosimeter ........................................... 2.3.3
Exposure Biomarkers for Reproductive and Developmental Toxicity .................. 2.3.4
Feasibility Study of the Reduction of Background Using Proportional Counter in
Coincidence ............................................................................. 2.3.5
Modeling of Images of the Human Body for Applications in Absorbed Dose Calculations ................................................................. 2.3.6
Non-Ionizing Radiation (NIR) Hazard Assessment Software ......................... 2.3.7
Use of Proliferating Cell Nuclear Antigen (PCNA) Assay to Quantify Cell
Proliferation in Respiratory Tract of Rodents Inhaling Chemicals or Radioactive
Materials .............................................................................. 2.3.8

2.4 Materials and Chemical Sciences

Analytical Atomic Spectroscopy Using Ion Trapping Techniques ..................... 2.4.1
Catalyst Design ...................................................................... 2.4.2
Laser-Induced Fluorescence in Multicomponent Refractory Oxide Hosts ............... 2.4.3
Material Structural Properties and Physics of Scintillators ............................. 2.4.5
Photoacoustic Laser Calorimetry for the Determination of Rate Constants ......... 2.4.6
2.5 National Security Technology

- Evaluation of Foreign Satellite Radar Data ........................................ 2.5.1
- Lithium Isotopes in Particles .............................................................. 2.5.3
- Remote Identification Research and Development .................................. 2.5.4

2.6 Reactor Technology

- Advanced Targets .................................................................................. 2.6.1
- Definition of Observables to Facilitate Transparency ............................. 2.6.2
- Eddy Current Methods/Applications Development ................................. 2.6.3
- International Reactor Safety .................................................................. 2.6.6
- Tools for Reactor Analysis ..................................................................... 2.6.7

2.7 Waste Technology

- CEPOD Treatment of Hazardous Organics ............................................. 2.7.1
- Destruction of Organics with Corona Discharge ..................................... 2.7.2
- Enhanced Bioremediation Using In Situ Heating ..................................... 2.7.3
- In Situ Vitrified Barrier Ring .................................................................. 2.7.4
- In Situ Vitrified Depth Enhancement and Subsurface Melt .................... 2.7.5
- Waste Processing Modeling and Innovation .......................................... 2.7.6

Acronyms and Abbreviations .................................................................... A.1
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 Field Office Manager. The report provided in this document represents Pacific Northwest Laboratory’s (PNL) LDRD report for FY 1992.

During FY 1992, 125 LDRD projects were selected for support through PNL’s LDRD project selection process. Total funding allocated to these projects was $11.9 million. This amount represented 3.2% of PNL’s operating budget, which is substantially below 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 to research related to our "core competencies." Currently, PNL’s core competencies have been identified as:

- integrated environmental research
- process science and engineering
- energy distribution and utilization.

In this report, the individual summaries of Laboratory-level 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.

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 $25K or less. The projects are described in Section 2.0.

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 and 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 importance to 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 capabilities. 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 which can be used to promptly pursue new ideas and concepts and enrich the Laboratory’s core competencies.

Program Benefits

PNL’s LDRD program and its predecessor, the Exploratory Research and Development (ER&D) program have provided a number of benefits relative to the generic goals of fostering creativity and innovation within the Laboratory. In addition, the program has 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/ER&D 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 significance of problems and issues associated with possible changes in the global climate and the environmental restoration of Hanford and other DOE sites is now well recognized. Scientists and engineers want to contribute to the solution of these problems, but often find themselves without an adequate mechanism to do so in an integrated and collaborative fashion. We regard PNL's LDRD program as an essential component of building such an integrated effort.

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 remediation technologies. 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/ER&D 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/ER&D funds and are now receiving programmatic support from DOE. Examples include previous LDRD/ER&D-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 materials 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/ER&D funding available to small, interdisciplinary teams of researchers with new ideas or concepts that require only a small amount of funding (typically less than $25K) 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 summary, LDRD/ER&D has enabled PNL to enhance its research vitality as a DOE multiprogram laboratory during a period of significant change. It has facilitated its 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 allocations for LDRD accounts are made by the Laboratory Director's Office. Primary responsibility for allocations to individual LDRD projects within these accounts rests with line and office managers, with oversight from the Senior Science Director.
All projects are reviewed for technical merit by line managers and/or scientific staff, and in some cases by external peer reviewers. Written guidance 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 Office of the Director of Strategic Planning. 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 on the next page. Additional details on these steps are as follows:

- Based on the approval of PNL’s LDRD Plan by the Secretary of Energy, initial funding allocations for LDRD accounts are approved by the Laboratory Director and disbursed by the Director of Finance. A portion of the total LDRD funds are retained for later distribution during the fiscal year.

- Line and 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.

- The emphasis required in 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 WBS is assigned by the LDRD Office for each LDRD project.

Primary responsibility for ensuring adequate technical review of LDRD projects rests with center and initiative managers. In addition, quarterly or more frequent reviews of selected projects may be performed under the leadership of the Senior Science Director. Bi-weekly seminar series are also 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 are also asked to participate in annual DOE LDRD program reviews, which are organized by the Director of Strategic Planning and the LDRD Office. The Director of Strategic Planning and the LDRD Office have primary responsibility for developing the annual LDRD Plan, with the concurrence of the PNL Senior Science Director and the Director of Finance.
Review and Allocation of Laboratory Overhead Accounts  
Responsibility: Laboratory Director's Office

LDRD Proposal Guidance Issued  
Responsibility: LDRD Office (Strategic Planning)

LDRD Project Proposals Solicited  
Responsibility: Center and Initiative Managers

LDRD Project Proposals Submitted and Approved  
Responsibility: Senior Scientist, Project Director, Center Initiative, Department, and LDRD Office (Strategic Planning)

PNL's LDRD Allocation Process
1.0 Laboratory-Level Projects
1.1 Integrated Environmental Research
A Novel High Resolution, High Sensitivity Infrared Technique for the Detection and Analysis of Gas Phase Molecules and Clusters

R. S. McDowell (Chemical Structure and Dynamics)

The focus of this project is to develop a powerful spectroscopic technique using cooled gas expanding from a slit nozzle, and high-resolution tunable semiconductor diode lasers to study metastable species and weakly-bound clusters. To use the technique, samples are prepared by entraining a solute in a carrier gas (i.e., helium, neon, argon, etc.) and allowing the mixture to expand into a high vacuum via a unique pulsed supersonic slit nozzle. The ensuing “ribbon” of gas is probed with the output of a tunable infrared diode laser (3.5 to 30 microns).

A relatively new spectroscopic technique was developed after last year to overcome three traditional problems that plague high-resolution gas-phase infrared spectroscopic techniques: spectral congestion due to the population of numerous quantum states in room-temperature gases, Doppler broadening of spectral features due to motions of the gas molecules, and pressure broadening that arises from the effects of molecular collisions. By cooling and reducing the pressure of a gas sample, these three effects can be minimized but at the expense of greatly reduced signal levels.

The technique employed here takes advantage of the effects of rapidly expanding a gaseous sample into a moderate vacuum. The gas is expanded through a slit orifice which measures 5 inches in length by 1/6000 inch wide. The resulting ribbon of gas expands at supersonic velocities and, in the process, molecules entrained in this gas are cooled to a few degrees above absolute zero. In addition, the random three-dimensional motion of the gas molecules is changed to a two-dimensional flow with little velocity component in the plane of expansion but perpendicular to the mass flow. If infrared laser light is used to interrogate the gas molecules through the plane of expansion, spectral congestion, Doppler broadening, and pressure broadening are all reduced significantly.

The interaction between sample and laser light is optimized by multi-passing of the laser light through the ribbon of gas. This is accomplished by incorporating a custom-designed multiple-reflection White cell optical arrangement into the vacuum chamber. Although the White cell increases our signal by about 30 times, it also introduces a small (0.01% of total laser power) pseudo-systematic noise component that cannot be removed by simple subtraction techniques. This noise is common to almost all White cells, and has been traced to étaloning effects within the cell. Recently, we developed a scheme for avoiding this étaloning problem by mounting one of the White cell mirrors on a piezoelectric translation stage. In effect, the optical path length of the White cell is randomly changed during data acquisition and hence averages out the sinusoidal noise. This innovation has given us an additional tenfold increase in signal-to-noise.

We have recently obtained high-resolution infrared absorption spectra of the Ar-N₂O dimer, whose intermolecular frequencies had been estimated from microwave data to fall near 40 cm⁻¹. The observed band is a combination of the intermolecular bend at 32 cm⁻¹ with the highest-frequency intramolecular stretching fundamental of N₂O at 2224 cm⁻¹. Despite the weakness of this band (some 200 times weaker than a typical vibrational fundamental), high-quality spectra were obtained with this equipment. Over 200 vibration-rotation transitions were observed and analyzed to determine the molecular constants. Certain anomalies in expected relationships between these constants indicate a limitation in the degree to which the vibrational and rotational motions can be considered independent. Such anomalies have been previously observed in low-frequency large-amplitude bending motions, and can provide insight into the exact nature of the molecular motions involved.

Such results are of general interest in helping to understand the weak forces that bond such clusters and that are responsible for the initiation of
condensation processes. They also are relevant to atmospheric modeling programs involving N₂O, a significant greenhouse gas.

Publications


Advanced Instrumentation for Materials and Interfaces

J. Janata (Materials and Interfaces)

This project was aimed at developing new capabilities to utilize recent advances in experimental instrumentation for application to problems in environmental chemistry. Target areas were solids nuclear magnetic resonance (NMR), electron microscopy, and surface chemistry, with an emphasis on developing capability to introduce samples without altering the natural chemistry.

A series of measurements were conducted critically testing the ability of advanced x-ray photoelectron spectrometers to determine the surface composition of small single crystals of layered materials. These tests showed both the major improvements that have taken place in instrumentation and current limitations of such methods.

A capability was developed for advanced testing and development of sensors. This capability is being utilized to develop sensors for tank environments.

Measurements of the surface structure (molecular and microscopic) of calcite were made using and testing atomic force microscopy. These methods have been shown to allow measurements in aqueous environments and can provide for observation of both growth and dissolution of minerals as they occur.

New knowledge was gained on the use of optical methods with submonolayer surface sensitivity for surface measurements. Such methods can be used in vacuum, liquid, or gaseous environments.

Publication

D. A. Cleary and D. R. Baer, XPS and ESR or SnSe₂ - 1 % (CoCp) ₃₆₆, Chemistry of Materials, 4 (1992) 112-116.
Advanced Separations and Mass Spectrometry

R. D. Smith (Macromolecular Structure and Dynamics)

The focus of this project was to explore advanced high resolution separation methods and advanced ultra-high sensitivity and extended molecular weight range mass spectrometric methods. The scope of this project involved investigations of the basic chemical and physical phenomena underlying the advanced analytical methods and vital for their further development, and the development of advanced instrumental concepts for obtaining improved sensitivity and detailed structural characterization of important Hanford-related environmental, biochemical (e.g., bioremediation), and health-related systems.

During FY 1992, this new LDRD project resulted in strong initial progress toward our goal of exploring and developing new instrumental methods for future research related to environmental cleanup activities. Our longer term aim is to develop improved understanding of reactions and interactions of biomolecules relevant to such diverse purposes as environmental cleanup by bioremediation, studies of the molecular-level interactions of Hanford-related pollutants and radiation relevant to health effects, and the development of new biomarkers of chemical and/or radiation exposure.

During this last year, our research was largely directed at development of methods and instrumentation for probing the structure of large biopolymers and the necessary ancillary methods relevant to their characterization (e.g., on-line separation methods, such as capillary electrophoresis, to make tractable the complexity inherent in most biological materials). Selected portions of our research program are summarized below.

The Use of Gas Phase H/D Isotopic Exchange Reactions to Probe the Structure of Protein Ions in the Gas Phase

New methods to probe the higher order structure of large molecules can potentially provide qualitative information on changes to the three-dimensional structure of important biomolecules using far less sample than currently required with existing methods. The recent development of "soft" ionization methods based upon electrospray ionization (ESI), allow the formation of multiply charged ions from large polypeptides and proteins, providing new opportunities for probing structural characteristics and reactivity. We developed a new method which invokes the use of thermal energy ion/molecule reactions of multiply protonated proteins with D₂O in order to probe higher order gas-phase structural differences. Our present results show that qualitative differences in gas-phase structure of multiply charged macromolecules can be probed using high pressure ion/molecule reactions.

Studies of the Coulombic Effects on the Dissociation of Macromolecular Ions

We developed new methods to study the thermal activation of electrosprayed ions using a heated capillary reactor. The design of the reactor makes it well suited for studies of gas phase kinetics of ions produced at high pressures. Our measurements during FY 1992 provided new insight into the role of coulombic forces upon the stability of large multiply charged ions. An important result of these experiments is finding reduced stabilities of the more highly charged ions. The magnitude of the activation energy lowering is similar to that predicted on the basis of simple models which we previously developed. This technique should be applicable to any method capable of generating ions at atmospheric pressure and is not limited to electrospray generated ions. Further refinement of the present apparatus should vastly improve the quality of the measurements, as well as broaden the scope of application. For example, development will require improved temperature control and temperature measurement, as well as methods for varying residence time.

The Study of Noncovalent Associations in Solution by Mass Spectrometry

Electrospray ionization was demonstrated to preserve noncovalent associations into the gas phase, providing a new approach to the determination of both non-specific and structurally-specific noncovalent associations in solution. A particularly important
model system was explored; base pairing of oligonucleotides (duplex), one of the most important and thoroughly studied noncovalent associations of biopolymers. In this last year, we have succeeded in developing methods for the ionization and detection of intact duplex oligonucleotides by negative ion ESI-MS. These results are the first observation of duplex oligonucleotides from solution by mass spectrometry, a potentially significant first step toward the study of more complex oligonucleotide and nucleic acid associations.

Development of Ultra-High Resolution ESI-Ion Cyclotron Resonance Mass Spectrometry

Many important applications of mass spectrometry to basic and applied research demand much higher resolution than that provided by conventional mass spectrometers. Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry offers a number of attractive features, combining nondestructive ion detection and the capability of very high resolution. The ICR method has the capability to trap ions for an extended time period, and allows numerous sequential m/z measurements to be conducted, a capability referred to as MS^n. The development of appropriate instrumentation combining the atmospheric pressure electrospray ionization process will open broad new research opportunities by providing the basis for the formation, isolation, and extended trapping of high molecular weight biopolymers and potentially even single highly charged biopolymer molecular ions (such as DNA segments) with molecular weights extending into the mega-dalton range. The new instrumentation consists of an electrospray ionization source interfaced to an external ion injection FT-ICR instrument and includes a number of novel features which have served to provide greatly enhanced resolution and sensitivity compared to earlier efforts at other laboratories. With this system, an electrospray ionization mass spectra can be obtained for ions trapped in the ICR cell under conditions in which the effects of pressure do not degrade obtainable resolution (i.e., in the 10^-10 torr range). Our initial results have demonstrated that coupling electrospray ionization with FT-ICR can produce high resolution (~400,000) for proteins in excess of 12 kDa molecular weight. The application of FT-ICR to large proteins, DNA segments, and other large species is expected to benefit dramatically from the application of this new tool due to its high resolution, high mass measurement accuracy, and flexibility for chemical reactions processes for purposes such as developing chemistry appropriate for sequencing.

Additional research efforts related to high resolution separations in small capillaries, large molecule dissociation processes, ion-ion reactions processes, and advances in high sensitivity analysis are included in publications which have resulted from this research.

Publications


Advanced Software for Molecular Science Computations

R. A. Bair (Theory, Modeling and Simulation)

Recent advances in computer technology offer opportunities to address new classes of molecular problems in environmental chemistry, materials science, and biochemistry. These increases in computational capability will enable studies of many "grand challenges" in molecular science. Likewise, advances in computer technology have provided computer graphics equipment capable of analyzing and displaying the vast quantities of information produced by large-scale molecular simulations, promising to significantly advance the scientist's ability to analyze research data. However, though impressive computer hardware is becoming available, present scientific applications software is not ready to take on the grand challenges. To address these software needs, this project was designed to develop a new generation of quantum chemistry and molecular dynamics computer codes for large-scale molecular science calculations on cost-effective massively parallel computer systems; integrated computer program and data systems with modern graphical user interfaces for molecular simulations, with a focus on the program systems above; and visualization tools for analyzing the massive amounts of data obtained from large-scale molecular simulations.

During FY 1992, prototyping projects were completed in each of the following technical areas.

Codes for Parallel Computer Systems

A benchmark Configuration Interaction code was written for the Intel Touchstone Delta in collaboration with Argonne National Laboratory (ANL), opening up much larger systems for scrutiny at this highest level of ab initio theory. A sustained computation rate in excess of 4 GFLOPS (4 billion floating point operations per second) was attained with 512 Delta processors. The prototype empirical force field code, PARADYN, was improved and benchmarked for the Intel Touchstone Delta system. Inter-processor communications performance of the Delta was found to be the limiting performance factor in scaling this replicated data method. Also in FY 1992 an existing augmented-plane-wave density functional code for studying solids, FLAPW, was parallelized. This code exploits distributed data structures, and calculations were performed to evaluate the applicability of density functional methods to Molecular Science Research Center (MSRC) research. Preceding work on parallel standard-SCF and direct-SCF methods was also extended, optimizing communications between master and slave processes, analyzing disk input/output performance using several approaches, and installing improved global operations.

Graphics and Visualization Codes

A significantly enhanced prototype for electronic structure code input was completed. The Computational Chemistry Input Assistant was enhanced to reference a database of computational and experimental results to provide advice on computational basis set parameters. Test computations were completed to populate the database. Also in FY 1992, visualization tools were developed to analyze electron densities from quantum chemistry computations on extended systems (e.g., periodic solids), and methods were developed to convert the computed electron densities into a form that could be used in molecular dynamics computations.

Integrated Code Systems

A study of the high level interactions between computational chemistry applications, their graphical user interfaces, visualization analysis, and databases was completed (in collaboration with scientists from Tektronix subsidiary CAChe Scientific, and the Oregon Graduate Institute). After considering several alternatives, an object-oriented approach was recommended, with object request brokers handling the communication of molecule objects between computers, and an object database for persistent molecule data storage.
Publications


Background Aerosol Optical Depths From Astronomical Archives

N. S. Laulainen (Atmospheric Sciences)

The purpose of this project was to glean light extinction data from a subset of the observatory sites used in the Project ASTRA work, compare these data with those obtained with solar radiometry, and subject this data to a variety of statistical analyses to evaluate trends and changes in the global atmospheric burden of aerosol particles. Prospective sites include Kitt Peak National Observatory (KPNO), Cerro Tololo Interamerican Observatory (CTIO), Lick Observatory, and McDonald Observatory. Of particular interest was data that had been collected from the early 1970s, after the publication of the ASTRA papers. Simple harmonic and trend analysis, as well as more complex statistical analysis procedures, such as LOWESS (locally weighted regression and smoothing scatterplots), will be applied to the data sets.

Several astronomers were contacted to identify suitable data bases on atmospheric light extinction obtained at various observatory sites that could be used to evaluate trends and changes, including seasonal variations and volcanic perturbations, in the distribution and global burden of atmospheric aerosol particles. One of the more complete data sets was obtained from Lowell Observatory in northern Arizona (Lockwood 1992, personal communication) and summarized in a journal article (Lockwood and Thompson 1986). The major activity of this LDRD project was to compare the results of the analysis of the Lowell Observatory (LO) extinction time series compared with a similar analysis performed for an overlapping time series of atmospheric optical depth measurements derived from direct beam solar radiation observation obtained at PNL's Rattlesnake Mountain Observatory (RMO) (Michalsky et al. 1990). The results of this comparison study were summarized in a journal article (Laulainen 1992). The significant findings of this study were (at 550 nm wavelength):

- The LO and RMO extinction time series showed a similar seasonal variation in light extinction, with maximum values occurring in the late spring to early summer and minima occurring in the winter months. The amplitude of the seasonal variation of optical depth at RMO (mean value = 0.025 was roughly twice that observed at LO (mean value of 0.015). The seasonal variability is attributed to aerosol mass loading changes in the lower troposphere as a result of biogenic and human activities and photochemical processes.

- Volcanic perturbations make a significant contribution to atmospheric aerosol optical depth. The El Chichon event in the early 1980s produced a mean optical depth change of 0.10-0.12 at the peak loading of the stratospheric aerosol layer, as observed over the LO and RMO mid-latitude sites.

Because of the manner in which the analysis was performed, no attempt was made to examine time trends in the time series from either the LO or RMO sites.

Other sources of data have been identified, but, as yet, no further analyses have been performed. Potential candidate astronomical observatory sites include Mauna Kea (Hawaii), KPNO (southern Arizona), CTIO (Chile), European Southern Observatory (Chile), an automated meridional photometric telescope at an observatory site in the Canary Islands, and a relatively industrially-impacted site in Brno, Czechoslovakia. Extracting data from these sources would require additional resources and time commitments working directly with the principal investigators who collected these data.

References


Presentation

Biodegradative Enzyme Design

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

A basic premise for undertaking a rational redesign research program is that "designing" multiple changes into an enzyme under laboratory-controlled conditions may be the only systematic and timely alternative to waiting for essentially geological time scales for such rare changes to occur in vivo under natural conditions. In order to have a reasonable chance to successfully carry out rational redesign, to alter a biodegradative enzyme's specificity and/or enhance its efficiency, it is necessary to have adequate structural data about the native enzyme and native enzyme-substrate interactions, an understanding of the underlying catalytic mechanism(s), a cloned gene for site-directed mutagenesis experiments, and reliable simulation methods for studying protein dynamic fluctuations. Studying the dynamic motions of relevant enzyme-ligand complexes for adequate time periods is necessary for rational redesign since an experimental (x-ray crystal or solution nuclear magnetic resources) structure is a static, time-and-space average structure. Joint theory-experimental studies of structure-function-dynamics relationships of the biodegradative enzyme cytochrome P450cam were used as the basis for rational redesign and genetic engineering for enhanced bioremediation of DOE-site contaminants. This research included computational modeling and simulations, site-directed mutagenesis, physical-biochemical characterization, and x-ray crystal structure determination. All of these activities focused on biodegradative enzyme redesign.

Cytochrome P450cam hydroxylates camphor-forming 5-hydroxycamphor with essentially 100% regiospecificity, while norcamphor is hydroxylated forming three products (45% 5-, 47% 6-, and 8% 3-hydroxy-norcamphor). Our previous simulations of norcamphor-bound P450cam predicted predominately (from 68% to 88%) 5-hydroxynorcamphor. One possible explanation for this discrepancy is that the simulations were performed using D-norcamphor, while the experiments were conducted with racemic norcamphor. The suggestion that norcamphor is the D-isomer was based on the similarity with the native substrate D-camphor. Indeed the reported crystallographic structure for norcamphor-bound P450cam models norcamphor as the D-isomer. Unfortunately, the two stereomers have never been separated. Three simulations each of the L- and D-isomers of norcamphor bound to cytochrome P450cam were compared to account for the effects due to substrate orientation and the assignment of random velocities. Our recent results show that the L-isomer of norcamphor is predicted to give rise to predominately 6-hydroxynorcamphor, while the D-isomer gives rise to mainly 5-hydroxynorcamphor. From this data, we infer that racemic norcamphor will give rise to non-racemic 5- and 6-hydroxynorcamphors after oxidation by cytochrome P450cam.

Before attempting to redesign the activity of P450cam for a substrate significantly different from camphor, we chose to first modify the specificity of P450cam for the substrate analogue norcamphor. Achieving such an intermediate goal will give us considerable confidence and guidance toward modifying the specificity of P450cam to initiate the degradation pathway for targeted pollutants. To date, we have made two predictions that were confirmed experimentally. The first involved mutating residue 87 based on the unexpected molecular dynamics simulation results indicating that this buried active site residue's very unusual dynamic mobility was correlated with the enzymes catalytic efficiency. Changing residue 87 from phenylalanine to tryptophan resulted in a 100% increase in coupling efficiency, in semi-quantitative agreement with the prediction. Our second successful prediction involved an alteration of specificity and efficiency of cytochrome P450cam hydroxylation of 1-methyl-norcamphor. The wild enzyme hydroxylates the 3, 5, and 6 positions of norcamphor, but only at the 5 and 6 positions of 1-methyl-norcamphor. For camphor, the degree of coupling is 100%, but for both norcamphor and 1-methyl-norcamphor, the efficiency is dramatically lowered to 12% and 50%, respectively. Based on modeling and simulation results, it appeared that mutating position 185 from threonine to phenylalanine would eliminate hydroxylation at the 3 position and dramatically increase
coupling. This mutant was constructed and the product profile and coupling experimentally determined. The coupling was doubled and hydroxylation at the 3 position was essentially abolished; both in agreement with the prediction.

Publications


Presentations


Carbon Protocol Analysis

J. A. Edmonds (Technology Management Planning)

The goal of this project was to increase the understanding of the primary factors responsible for the rapid growth in emissions forecasted for the developing world. The project has produced estimates of carbon emissions by region and through time under a variety of assumptions about GDP growth, participation in a compact to lower carbon emissions, and technology transfer from the developed to developing world.

The special version of the ERM was successfully completed during 1992. Analysis using the model has also been completed.

An overall conclusion resulting from the study is that any agreement to control fossil fuel carbon emissions, no matter how skillfully crafted, will require a process of constant revision in terms of participation. This result is not simply because the natural science will be changing, but because the economic needs of its participants will be evolving. Additional conclusions included the following:

- Costs of individual national emissions targets leading to a stabilization of global emission, will be much higher than the costs to participants of efficient instruments such as a carbon tax or tradable permit. Overall costs of individual national targets were approximately double those of an efficiently administered global target, though costs to developed nations were actually lower.

- Conventional "equity" based principles, such as equal per capita emissions rights, for allocating tradable permits may either,

  - transfer too little wealth to developing nations, leading to a "dropout" problem, or
  - raise costs to developed nation participants to unacceptable levels.

- Full participation by the world's nations may not be necessary to achieve most of the results of "full participation." Perhaps as few as a dozen nations may be able to control atmospheric carbon concentrations.

- Accelerated technology development and deployment to developing nations may greatly reduce costs.

- Short delays, on the order of 10 to 15 years, in establishing an agreement may yield only small differences in long-term atmospheric concentrations.

Presentations


The meeting Prospective Modeling, Decision Criteria and International Negotiation on Sustainable Development: The Case of Climate Change, organized by Centre National de la Recherche Scientifique; Paris, France, October 25-30, 1992.

Chemical Adducts and Radiation Sensitivity of Supercoiled DNA

J. M. Nelson (Biology and Chemistry)

This project was directed toward investigating the effect of DNA adducts on the radiation sensitivity and the location of DNA damage induced by ionizing radiation in torsionally stressed DNA plasmids. DNA plasmids are to be constructed that contain a single adduct at a defined sequence location in a restriction fragment and that can be isolated after irradiation. The plasmid into which this construct is inserted will be produced with varying degrees of superhelicity to provide one of the basic tools needed to investigate the relationship between DNA structure and radiation sensitivity.

The specific goals of this project were: 1) to detect and map the location of altered DNA structures, 2) to synthesize oligonucleotides containing the novel DNA structures and splice them into plasmids, 3) to supercoil the DNA, thereby generating the torsional stress in these hybrid constructs, and 4) to very accurately determine the form of the plasmid containing the structurally altered DNA, in order to quantify x-ray sensitivity.

Considerable progress has been made in three of these areas. We have shown that altered structures occur in the plasmid we are using, pIBI30, and have mapped their location. The methods and techniques developed in the course of this work apply directly to work with other plasmid systems.

We have identified the conditions required for supercoiling plasmid DNA and generated families of plasmids with different superhelicities. This work has been done with the plasmid pBR322. Again, the techniques developed are directly applicable to other plasmids.

We have also been developing methods to accurately determine the quantity of plasmid DNA in various forms (plasmid DNA can be in three forms: Form I - intact, supercoiled DNA; Form II - nicked, relaxed circular DNA; and, Form III - the linear DNA molecule), using two different approaches. We are

1) investigating ways to enhance the precision of Southern blotting methods to quantify plasmid DNA, and 2) developing an high-performance liquid chromatography method for separating and quantifying the different plasmid forms. We are confident that one of these methods will provide accurate quantification of plasmid DNA.

Because we have not yet worked out the necessary techniques, we have not made progress in the synthesis of plasmids containing inserts containing perturbed structure.

Using Mung-bean nuclease and five different restriction enzymes, we have now demonstrated that spontaneous single-strandedness occurs naturally in the AT-rich region, between bp 2000 to 2050, identified by Benham (J. Chem. Phys. 92: 6294-6305, 1990) from theoretical determinations based on primary structure. Mung-bean nuclease cuts only one strand of double-stranded DNA, within a single-strand or denatured region. We also learned that Mung-bean nuclease will cut the second strand, if given sufficient time and slightly more aggressive digestion conditions. As a result, a second nuclease digestion to cut the single strand was not needed.

The location of these nicked single-stranded regions was then determined by cutting the plasmid with a restriction enzyme that recognizes a unique sequence and cuts the DNA at a defined location. We have used five different restriction enzymes that cut the pIBI-30 plasmid at distinctly different unique sites, (i.e., at only one place on the molecule: EcoR1 @ bp 276, Hind3 @ 336, Dra3 @ 772, Xmn1 @ 1313, and Sca1 @ 1432). If the Mung-bean nuclease nicked the molecule at or within a single region, then each restriction enzyme should produce fragments of defined lengths. The lengths of the fragments found were virtually identical to those lengths predicted had the nuclease nicked the DNA at the AT-rich region around bp 2000.

In addition to developi... the methods employed, these experiments have shown us that the native supercoiled
plasmid is naturally single stranded, at least part of the time, at that location which corresponds precisely with the region predicted by Benham (J. Chem. Phys. 92: 6294-6305, 1990), and where we observed enhanced radiation-induced strand scission (PNL Annual Rept., Pt. 4, Physical Sciences, pp. 57-61, 1992).

We have also been attempting to adapt Southern blotting methods coupled with 32P end-labeling procedures that can be used to corroborate the earlier studies that showed enhanced radiation damage around bp 2000. Experiments using these methods are in progress, but the results to date have not been satisfactory.

Presentation

Chemical Processes at Interfaces

S. D. Colson (Chemical Structure and Dynamics)

This project was designed to provide new capabilities and knowledge in the area of condensed phase chemical processes. Existing equipment, including a laser ionization mass spectrometer, was reconfigured and augmented to allow studies to be made of chemical reactions at surfaces under conditions common to chemical processing and in nature. Scientific issues being addressed in the project included the identification of key chemical routes for surface-controlled environmental clean-up processes, development of novel physical methods for the study of surface processes, an improved understanding of the reaction mechanisms important to chemical processing, and identification of catalytic processes important to the treatment of DOE-stored wastes that are in need of mechanistic study.

During FY 1992, an extensive study was carried out of the catalytic oxidative coupling of methane, a process that leads to the formation of gas-phase methyl radicals and C2 hydrocarbons. A microreactor was designed to quench the reaction via a supersonic expansion into a vacuum; the resulting rapid cooling and greatly reduced collision rates allow even very reactive species to be ionized and detected by laser ionization mass spectrometry (LIMS). The apparatus is also equipped with a quadrupole mass spectrometer for the detection of all other reactants and products.

This study focused on the kinetics of methyl radical formation on a 1% Sr/La2O3 catalyst bed as a function of reactor temperature. An existing catalyst bed was modified to minimize pressure gradient and residence times, thereby avoiding secondary reactions. The results demonstrate that methyl radical formation increases with temperature over the range 500 to 1000°C, with an apparent activation energy of 20 kcal/mole. At all temperatures the methyl-radical yield is zero order in O2 and first order in methane. These data are consistent with the reaction mechanism

\[ \text{O}_2(\text{g}) + 2\text{S}^- \rightarrow 2\text{OS}^- \]
\[ \text{CH}_4 + \text{OS}^- \rightarrow \text{CH}_3(\text{g}) + \text{HOS}^- \]

where S- represents an active site on the surface. The active sites are regenerated by recombinative desorption of surface hydroxyls to form water.

In related experiments, we have demonstrated that a previously-observed maximum in methyl-radical production at 800°C arises from depletion of OS-sites along the reactor bed, due to insufficient gas-phase O2 to maintain the heterogeneous equilibrium.

These results demonstrate that the equipment developed here can provide data to elucidate the kinetics and mechanisms of condensed-phase reactions. They also have clarified the nature of the important methyl-radical formation process on catalytic surfaces.

Publication

A manuscript for a journal article on the kinetics of methyl radical formation on metal oxide catalysts is being prepared.
Chemical Sensors and Interphase Chemistry

J. Janata (Materials and Interfaces)

The goal of this project was to develop a new capability to examine, at the microscopic level, relationships between the structure of environmentally relevant interphases and the kinetics and thermodynamics of processes occurring in these regions, and develop the understanding required for the rational chemical and physical modification of surfaces for desired interphasic behavior. This work is critical to establishing the basis for a new sensor development program.

Two hundred suspended gate field-effect transistors (SGFET) have been designed and fabricated in collaboration and under a subcontract with the University of Utah. They will be used for development of solid state gas sensors. During the SGFET fabrication an important process step has been developed that may facilitate fabrication of other types of chemical sensors. It pertains to photolithographic patterning of noble metals on the scale of 4-5 micrometers.

Fabrication of twelve prototype quartz crystal microbalance probes has been completed and initial testing proved that their performance meets the expectations. Namely, it is possible to operate these probes as two independent oscillators in either liquid or gaseous media.

A review on chemical sensors has been published. It is based on an extensive database containing over 1800 references of chemical sensor publications in the last 2 years. This database has been made available to other researchers at PNL.

Reference


Presentations


Child Health and Welfare Index

J. D. Longstreth (Technology Management Planning)

The objective of this project is to develop a model for assessing the health and welfare status of human populations for application in deliberations on the possible impacts of global climate change. This involves refining initial efforts, which resulted in the development of the Child Health and Welfare Index - a method for ranking countries on the basis of the status of children, and then exploring possible ways to connect this index to the Second Generation of the Edmonds-Reilly Model (SGM).

During FY 1991, we explored the idea of developing a model for assessing the health and welfare status of human populations which could be used to integrate this concern into planning activities for global climate change. Preliminary work indicated that the development of such a model, predicated on an assessment of the health and welfare status of children was possible, and the Child Health and Welfare Index (CHWI) was created using several sources of data and seven data elements.

In FY 1992, this concept was expanded to include nine data elements which allowed introduction of better metrics for assessing nutritional status and access to clean water. The choice of the nine elements was achieved via several types of analysis (e.g., principal component analysis), resulting in a much more robust model. On the basis of this second version of the CHWI, 145 countries were ranked.

During FY 1992 we also began to explore linking the CHWI to the Second Generation Edmonds-Reilly Model (SGM). Since the SGM is divided into nine regions, the first step was to aggregate the information from our 145 countries into the nine regions, taking care to ensure that the same aggregation techniques were used in the CHWI as are being proposed for the SGM. Preliminary discussions with the SGM team were begun in order to explore possible connections between the SGM and the CHWI so that when the SGM predicts the economic impacts of global climate change, those predictions can be linked to the CHWI to indicate potential changes in the health and welfare status of human populations.
Computer Modeling of DNA Perturbations

J. H. Miller (Biology and Chemistry)

The objective of this project is to develop computer-based molecular modeling techniques that complement evolving experimental studies of DNA damage by radiation and chemical insult. Ab initio quantum mechanical methods are used to calculate the minimum energy conformation of modified DNA subunits (base, sugar, and phosphate groups) and the forces that couple these moieties to the macromolecule and its aqueous solvent. Molecular dynamics simulations (MDS) are used to obtain relaxed macromolecular structures that model the radiation- or chemically-induced lesion in a defined sequence context. Structure-function relationships are derived by investigating the interaction of damaged DNA with enzymes involved in DNA replication and repair. These structure-function relationships play a key role in our understanding of the consequences of DNA damage at higher levels of biological organization and thereby contribute to the scientific basis for assessing health risks from radiation and chemical exposure.

Technical progress was made in the following areas: 1) comparison of two closely related thymine (T) lesions, thymine glycol (Tg) and dihydrothymine (dhT), 2) mispairing of 8-hydroxyguanine (8-oxoG) with adenine (A), and 3) modeling the active site of P1 exonuclease, an enzyme used in detection of base damage. Both Tg and dhT are modifications of T that saturate the C5-C6 double bond; however, the biological effects of these lesions are very different. Tg exhibits the characteristics of a bulky DNA lesion but dhT does not. This difference is due to electrostatic forces within Tg that cause the C5 methyl group to change its orientation relative to the pyrimidine ring.

In the axial orientation preferred by Tg, C5 methyl interferes with intrastrand stacking in normal B DNA. MDS of the hexamer d(CTAoxoGTC)d(GAATAG) suggest that oxoG:dhT mispairs can be very stable. This finding correlates well with experimental observations that oxoG:dhT mispairs are resistant to both proofreading by DNA polymerases and post-replication repair by glycosylase activity. Hence, anti-syn isomerization appears to be a critical step in the mutagenic pathway of 8-oxoG lesions. The limited amount of atomic-resolution experimental data on DNA polymerases and repair enzymes severely restricts our ability to model the DNA-protein interactions that are critical to understanding the biological effects of DNA damage. To circumvent this difficulty, we investigated the potential for modeling an enzyme-active site from sequence and functional homology. The nuclease *Penicillium citrinum* P1 was undertaken as a test case due to the large body of experimental data on other nucleases with similar catalytic mechanism and the availability of data on P1 specificity to test our results. An atomic-level model of the P1 active site has been developed and MDS of the binding of native and damaged dinucleotides to the site are in progress.

Publication

A manuscript describing our findings for the structure of Tg and dhT lesions has been submitted for publication in the *International Journal of Radiation Biology*. 

Integrated Environmental Research 1.1.20
Computing and Information Sciences Hardware

J. R. Lewis (Computing and Information Sciences)

Advances in computer technology offer opportunities to address many problems in the scientific realm. However, taking advantage of these opportunities requires research into the computational infrastructure for a scientific computing environment. The scientific computing environment requirements differ significantly from the standard user environment and dictate an innovative solution for an integrated environment. These requirements involve preconceptual design and applied research in: network design, distributed computing environment, scientific data management, and electronic circuits and computer interfaces for research instruments.

The technical progress on this work was significant in many areas during FY 1992. A scientific computing infrastructure was established which will be a conceptual baseline for future application at PNL and at other DOE laboratories.

A major accomplishment in the scientific computing environment infrastructure was the establishment of a Distributed Systems Test and Evaluation laboratory that provides a testbed environment for new and emerging distributed computing technologies. Technology and design concepts that were evaluated included the Andrew File System (AFS), high-performance network routers, and sizing and placing of network servers for best performance. Concepts were developed to implement a novel approach to network architectures. Under this concept, users in the PNL Math Building were segregated into small work groups and placed on an Ethernet subnet. Providing few users with extensive use of Ethers 10 Mbps bandwidth resulted in higher performance.

The computer instrumentation and electronics work involved the design and implementation of data acquisition and control systems and support of instrument development. Software was developed to perform functions such as control of optical delay lines and display of spectra data. Preliminary investigations were performed to determine how best to develop UNIX device drivers to CAMAC hardware.

A significant part of a scientific computing infrastructure involves the hardware configuration for storing the scientific data. Several technical approaches were investigated. Staff members became involved in the ongoing effort on the IEEE Mass Storage Model. This model appears to be the emerging standard and studies were performed to determine how this model can be implemented in a molecular science environment. This project was completed in FY 1992.
Computing and Information Sciences Software

J. R. Lewis (Computing and Information Sciences)

Advances in computer technology offer opportunities to address many problems in the scientific realm. However, taking advantage of these opportunities requires research into the computational infrastructure for a scientific computing environment. The computational infrastructure involves the integration of hardware and software that assists the scientists in acquiring, managing, analyzing, and distributing the data (both real and theoretical). As massively parallel and distributed computer systems have assumed a preeminent role in high performance computing, more emphasis must be placed on methods and tools to support the development of codes that can effectively use the capabilities of these machines. Increased performance on these machines typically leads to larger problems being solved. Visualization can be a powerful tool to analyze the results of scientific analysis. In the scientific data management realm, the goal is to understand the requirements for the collection and storage of information about the scientific data (meta data) and determine how to store self-describing information with the data files so that there is an easy transfer of data between applications.

Work in the high-performance computing arena involved continued participation as active members in the Concurrent Supercomputing Consortium, research in parallel eigensolver methods, performance modeling of parallel programs, and characterization of communication bottlenecks in message-passing parallel computers. The methodology developed in this LDRD project for modeling performance of deterministic message-passing programs was a key component in PNL’s proposal for a HPCCI Grand Challenges project that was funded by DOE.

Scientific visualization work involved the development of a software application to model and visualize crystal structures. The software uses the computer code written by MSRC scientists to mathematically build crystals, but enhances the code by graphically linking results into the Application Visualization System (AVS) so that long lists of numbers are replaced by three-dimensional view of crystals. This software was demonstrated at the First International AVS Users Group Conference.

Different classes of Graphical User Interface (GUI) development tools were examined including GUI Builders, Interface Development Tools (IDTs), and User Interface Management Systems (UIMS). Effort was directed towards identifying those areas of GUI development that current technology tended to support along with those which require additional research and evolution.

Scientific data management work continued on the development of a preliminary computational information model. The work focused on using object-oriented technology to determine how the data for computational chemistry could be structured and stored in a way that facilitated future use of the data. A small model was developed for ab initio data.

This project was completed during FY92.
Contaminant Risk Evaluation and Management

E. A. Jenne (Geosciences)

Research, methodological developments, and planning for a demonstration of an integrated risk assessment capability were carried out to enhance our understanding and capabilities in chemical and radiological risk assessment. Research has focused on resolving problems in assessing risk from multiple agents and alternative health-effects endpoints. An all-inclusive risk assessment/remediation/perception project was planned. Linkages with several other programs have been developed to provide a capability for a science-based, integrated estimation of the various health-related risks to the general population from contaminants present in the environment and to the worker population during remediation.

In FY 1992, the research efforts of this project were focused on combining risks from a variety of contaminants and endpoints, and predicting effect antagonisms or synergies among contaminants.

The basis for the evolving research program was prepared with separate literature reviews/overviews of "aggregate" risk assessment, and "comparative" and "relative" risk. Although there have been a rather large number of organism and cellular studies involving more than one toxicant, there has been little attempt to integrate these results. Therefore, a major bibliographic search of multiple agent studies was carried out. Because of the large body of literature found in the search, the focus was narrowed to two organic compounds, carbon tetrachloride and trichloroethylene, which are major toxicants at a potential demonstration project site. Building on this bibliographic review of organic compounds, a pragmatic, empirical modeling approach for complex organic mixtures was developed based on cellular and molecular studies. The bibliographic study was also used for a preliminary reevaluation of a possible linkage between teratogenesis and carcinogenesis that could be used to supplement the database currently available in each of these areas. In view of the large body of literature in aquatic toxicology, the literature in this field was interrogated for information and insight that it might provide relative to modeling toxicant interaction effects in higher organisms.
Cytofluorimetric Applications for Identifying Altered Molecular Markers

R. E. Weller (Biology and Chemistry)

This project is focused on developing and establishing methodologies for detecting, imaging, and measuring the potential usefulness of specific organic molecules at the nuclear, cytoplasmic, and membrane level as reflections of DNA structural changes. These methodologies may provide biomarkers of interaction of a host system with its environment. At the nuclear level, we will develop cytofluorimetric assay systems capable of detecting the induction of chromosomal alterations and/or damage using specific labeled probes, and develop techniques for imaging and quantitating the expression of those changes. At the cytoplasmic and membrane levels, cytofluorimetric assay systems will be developed to provide tools for elucidating molecular markers using monoclonal antibodies, other labeled probes, or dyes specific for distinct epitopes.

Monoclonal antibodies for staining MHC Class I and Class II (DP, DQ, and DR) antigens, as well as antibodies for helper, suppressor, and NK cells were obtained. We initiated the collection of additional information to relate exposure to gamma rays (60Co) and modulation of MHC Class II markers associated with the regulation of both humoral and cell-mediated immune function. We also conducted preliminary cytofluorimetric assays using monoclonal antibodies and nonhuman primate mononuclear cells in order to validate methodologies and procedures for the flow cytometer prior to initiating experiments. Further work was delayed until the postdoctoral appointee for this project is located at PNL.
Development of Tunable Ultrafast Laser Sources for Studying Real-Time Chemical Dynamics

X. Xie and G. Holton (Chemical Structure and Dynamics)

A state-of-the-art capability to generate ultrashort (100 fs) pulses tunable throughout the ultraviolet, visible, and chemical infrared regions is being developed. The system consists of a modelocked Ti:sapphire laser amplified with a novel all-solid-state Ti:sapphire regenerative amplifier. The tunable output is suitable for studies of the real-time dynamics of condensed-phase chemical and biochemical systems.

Understanding the influence of solvents on chemical reactions requires a knowledge of liquid structure and dynamics. The structure of a molecular liquid is a dynamic one, undergoing constant fluctuations. For example, in liquid water, hydrogen bonds dissociate and reform on a picosecond time scale. The infrared absorption band in the O-H stretching region is very broad, mainly due to different types of hydrogen bonding. Spectral "hole burning" experiments in this spectral region can be used to study the inhomogeneity and the distribution of hydrogen bonding. However, on the nanosecond or longer time scale, the system should always be homogeneously broadened. In order to probe the "transient structures," femtosecond infrared pulses are needed. Questions concerning structure and fluctuation of fluids at the subpicosecond scale are important, for on a single-molecule basis chemical reactions occur at this time scale. Nonlinear femtosecond infrared spectroscopy is an attractive approach for studying the dynamic structures of liquids and their influence on the transition states of chemical reactions.

We have designed an ultrafast laser system that will provide a unique combination of high peak power, high repetition rate, broad tunability in the visible and near ultraviolet, high temporal resolution, and good stability. It will meet many of the spectroscopic requirements for studying interfacial and solution-phase molecular dynamics: temporal widths in the 2- to 0.1-ps range, repetition rates of 1 kHz, 200 kHz, or 76 MHz, and high pulse energy.

This system employs a commercial modelocked Ti:sapphire laser that provides <100-fs transform-limited pulses at a 76-MHz repetition rate, with several-hundred-mW average power and tunability over the region 720–960 nm. The output of this system can be used directly in upconversion experiments. The small pulse energy available from this laser (a few nJ) will be amplified to meet the needs of such condensed-phase experiments as transient absorption and Raman, infrared, and nonlinear spectroscopies. This is accomplished with an all-solid-state Ti:sapphire regenerative amplifier based on a commercial Q-switched Ti:sapphire system. The fundamental and second and third harmonics provide a high-energy source tunable over most of the ultraviolet, visible, and near-infrared regions for a variety of condensed-phase ultrafast experiments. Ultrashort pulses in the chemical infrared region, especially around three microns, where absorption due to hydrogen stretching modes and hydrogen-bonding interactions are found, will be generated by synchron-pumped OPO and amplified by OPA.

The advanced conceptual design of this system has been finalized. It is anticipated that this equipment will give us unsurpassed capabilities for studying the structures and dynamics of liquids.
Earth and Environmental Sciences Research Related to Global Change

M. J. Graham (Earth and Environmental Sciences)

The objective of this project was to promote small research projects within PNL's Earth and Environmental Sciences Center that may lead to significant conceptual advancements in support of Global Change programs. Projects were principally focused on measuring or evaluating environmental effects of global climate change.

Specific tasks supported in FY 1992 included:

- **Global Climate Change and Sea Level Rise Effects on Coastal and Estuarine Habitats**<sup>(a)</sup>

- **Remotely Piloted Vehicle for Global Climate Change Measurements**

- **Driving PNL's Global Chemistry Model with Meteorological Fields from the National Weather Service's Medium Range Forecast Model**<sup>(a)</sup>

- **Remote Sensing of Plant Stress: Correlations with Plant Biochemical Processes.**

Global Climate Change and Sea Level Rise Effects on Coastal and Estuarine Habitats

During FY 1991, primary work focused on collection of cores in marshes for determination of sedimentation rates. In FY 1992, primary work consisted of establishing sites for determining potential effects of sea level rise on marsh productivity and detritus flow. These sites will require monitoring through FY 1993. In addition, a strong data set was gathered on eelgrass photosynthesis vs. light level from field and lab experiments. In FY 1992, we acquired the model developed for U.S. EPA for assessing the effects of sea level rise on the distribution of coastal habitats. We now have a good working relationship with its developer and have the ability to use and improve this model. Initial experiments were conducted on the effects of increased CO₂ on the photosynthetic rate of eelgrass and kelp. These experiments showed a strong positive increase in photosynthetic rate. The results have been discussed with GCC program managers at DOE-Headquarters.

Remote Piloted Vehicle for Global Climate Change Measurements

The initial approach has been to investigate the availability of component subsystems that can be assembled into a working prototype that can carry radiometric, aerosol, and meteorological sensors. The initial focus of the work has been on the remotely piloted vehicle (RPV) rather than the meteorological instrumentation. During the first year, tasks included: determination of aircraft type and design, size, weight, mission length, and field requirements; procurement, assembly, and designing the interfacing of selected RPV sub-systems; and ground-based testing of integrated RPV system components.

A special slow-flying push-prop model aircraft has been purchased and modified for our use. Such aircraft have been used in the past by the motion picture industry. This plane has a large pod at the front of the fuselage for radio control equipment and scientific instruments.

We received all major hardware components of the RPV in FY 1992, including the airframe, the autopilot, radio control electronics, on-board computer, data collection system and data storage modules, electronic compass, and Global Positioning System (GPS). In addition, we have purchased some auxiliary electronics, including a Motorola 85 single-chip processor which will be used as a flight recorder/controller. The GPS has been successfully tested.

(a) These tasks were formerly designated as LDRD projects -- Sea Level Rise Effects (P891032/666) and Driving PNL's Global Chemistry Model (P891018/652).
along with the compass, the computer and the computer interface to a PC. Algorithms are being developed to control the position of servos so that the aircraft can make turns under on-board computer control. The airframe, motor, and remote control electronics were tested in a flight in July. This initial flight resulted in a crash and made us aware of some shortcomings in the airframe design, which have now been modified.

The conceptual design of the RPV is 100% complete, and the detailed design is now 40% complete. During FY 1993, efforts will focus on the completion of our detailed design, integration of the sub-systems, completion of flight tests, incorporation of meteorological sensors, and writeup of a conference paper.

Driving PNL's Global Chemistry Model with Meteorological Fields from the National Weather Service's Medium Range Forecast Model

The Global Chemistry Model (GChM) is driven with wind fields provided externally. The objective of this project is to demonstrate the feasibility and utility of using meteorological fields produced by the National Weather Service's (NWS) Medium Range Forecast Model or the European Center for Medium-Range Weather Forecasting's (ECMWF) model to drive GChM. This capability would allow GChM simulations of actual meteorological episodes and longer time periods to be used for supporting field studies and interpreting the results of long-term monitoring programs. In FY 1992, through collaborations with Brookhaven National Laboratory and the University of Kentucky, access was obtained to software that will process the NWS and ECMWF data for use by GChM.

Remote Sensing of Plant Stress: Correlations with Plant Biochemical Processes

Initial experiments performed in this project with the herbicide fluridone (1-methyl-3-phenyl-5(a,a,a-trifluorom-tolyl)4-pyridone) that inhibits pigment (carotenoid) formation in the chloroplasts of the plant leaves demonstrated reflectance changes, particularly between 680 to 710 nm or in the so-called "red-edge" portion of the spectrum (Horler 1983). These reflectance changes also corresponded with increased stress marker enzyme, glutathione reductase (NADPH) glutathione oxidoreductase (E.C. 1.6.4.2) (GSH Reductase) activity.

These observations also demonstrated a consistent shift of this edge toward the blue portion of the spectrum within 4 to 5 days following application of the herbicide. This shift however was not as evident in plants exposed to glyphosate, a herbicide which inhibits synthesis of branch chain amino acids and subsequent protein synthesis. As a potential explanation for this, we hypothesized at the close of the fiscal year that the reflectance shift toward the blue may be at least in part promoted by the fluorescence of the chloroplasts within the leaves themselves.

The approach in FY 1992 employed bush beans (Phaseolus vulgaris, var. Tendergreen) grown in soil/potting mix combination (2:1, Burbank:Pro-Mix BX) in a greenhouse. The plant roots of the soil grown plants were exposed to three herbicides: fluridone, glyphosate, and DCMU (3-(3,4-dichlorophenyl)-1,1-dimethyleurea) (a Photosystem II electron transport inhibitor) both individually or in combination. Leaf reflectance measurements were made under a standardized light source, geometry, and neutral background with PNL's state-of-the-art Deadalus Portable field Spectroradiometer at 0°, 1° and 2°-days post-exposure. Following leaf reflectance measurements, leaf fluorescence (decreases in PS II efficiency), and leaf chlorophyll content (total chlorophyll and chlorophyll a/b ratios) were measured to determine correlations between stress levels and potential shift in the "red edge".

Four out of five experiments which employed DCMU and control plants indicated that an average rise in the per cent reflectance at 690 nm of from 5% to 30% was evident, particularly in the younger leaves of the plants after 24- to 48-hour exposure. PS II efficiency was decreased by 30% to 50% with a corresponding rise in leaf fluorescence in these leaves as compared to control levels. No significant loss in total chlorophyll content or change in chlorophyll a/b ratios was observed.

Plants exposed to fluridone at an identical concentration in 2 out of 3 experiments demonstrated a much lower (3% to 7%) increase in per cent reflectance after 48 hours with no significant loss in PS II efficiency (increase in leaf fluorescence). Further, there was no significant change in total chlorophyll content or chlorophyll a/b ratios during this time.

The evidence to date indicates a correlation between rise in per cent leaf reflectance at 690 nm with an increase in leaf chlorophyll fluorescence (decreased
PS II efficiency. There was no correlation over the short exposure time employed with loss of leaf chlorophyll or chlorophyll composition. Unfortunately these observation were made under greenhouse conditions. When the plants were transferred outdoor for similar measurements under direct sunlight, most of the variation in reflectance was lost. Confirmation of these results under field-grown conditions and within entire canopy structures will have to be addressed in future studies.

Reference

Publications and Presentations

Global Climate Change and Sea Level Rise Effects on Coastal and Estuarine Habitats

A publication is now in press in the journal *WETLANDS* which documents accretion rates vs. sea level rise rates. The results of the accretion rate studies were presented at the Global Wetlands conference in Columbus, Ohio, in September 1992.
Ecological Modeling

L. E. Rogers (Environmental Sciences)

The objective of this project was to facilitate the advancement of ecologic modeling. The project was planned so that ecological-atmospheric interaction models could be developed for interfacing with global change models. These models should consider the twin factors of economics and energy policy and be usable via a scaled version of a work station that concurrently incorporated other simulation and artificial intelligence (AI) models, as well as data sets (including input from Geographic Information Systems [GIS]).

A preliminary survey of ecological models potentially useful for global change studies was completed. The survey revealed that a large number of ecological/agricultural models were of marginal usefulness and very few models were explicitly constructed for linkage to Global Climate Model (GCM) or regional scale atmospheric models. Models with energy or economic components generally did not have an ecological component, nor can one be easily added. The principal models used to represent ecological-atmospheric interactions in global climate models were identified, and their capabilities and limitations were assessed. At least twenty land surface parameterizations are currently in use or development and none have a realistic ecological component due to space and time scale problems. In addition, there is inadequate modeling of ecological process changes and the resulting modifications in spatial patterns of vegetation types. The theoretical basis for phase transition modeling was investigated and a modeling design, preliminary programs, and input parameter estimates were developed for a model of natural vegetation changes due to future climatic changes in the Pacific Northwest. Two manuscripts for publication were outlined and partially drafted.

As part of the research effort, the SPUR-91 Rangelands Computer Model from U.S. Department of Agriculture (USDA-ARS) and the Century Soil Organic Matter Computer Model from Colorado State University were obtained and made operational on an IBM PS/2 Model 90/xP486, 25mhz desktop computer obtained for this program. In order to conduct ecological response analyses based on bifurcation-catastrophe mapping and nonlinear dynamics modeling, appropriate software for the PC was obtained. Modified parallel processing equipment for a Macintosh II computer was sent to Texas A&M University (a project collaborator) to make it available for use on a desktop machine. Finally, computer tools for linking ecological models with GIS have been developed and are being verified and tested for usability.

A FORTRAN computer model for generating global potential evaporation data from the Leeman's global database at 0.5 by 0.5 degree Latitude and Longitude for implementation in GRASS4-GIS was produced, documented and tested. This model was used in the development of a land use agricultural model by PNL researchers for developing the revised Energy-Economics Ecology model. The Dutch IMAGE Carbon Cycle model was revised for use in the Edmonds' model for carbon storage and biogenic emissions being developed for twenty global economic regions. Specifically, in this project, the code for changing the carbon cycling Terrestrial Biosphere module was changed so that it would operate on twenty regions of the globe instead of a single point.

The database on wildlands ecology modeling now contains over 3000 references. The entire Focus-On-Global Change disk-based database was searched and appropriate papers entered into the PNL system.
Enzymatic Transformation of Inorganic Chemicals

H. Bolton (Environmental Sciences)

The objective of this research is to investigate microbial immobilization of radionuclides and metals via redox induced precipitation or direct enzymatic alterations in oxidation state. Some of the dominant mobile groundwater contaminants at DOE sites have various oxidation states conducive to redox controls including uranium, chromate, Co(III)-EDTA, and pertechnetate. The reduced oxidation states of these metals have decreased mobility in the environment. This work uses iron-reducing bacteria, which can use Fe(III) as the terminal electron acceptor for metabolism and reduce it to Fe(II), to investigate the direct microbial enzymatic reduction of uranium, chromate, and Co(III)-EDTA.

Work in FY 1991 focused on determining the range of heavy metals which can serve as potential terminal electron acceptors for the iron-reducing bacteria. Results demonstrate that iron-reducing bacteria converted $^{14}$C-labeled lactate to $^{14}$CO$_2$ under anaerobic conditions with either iron [Fe(III)], uranium [U(VI)], chromium [Cr(VI)], or vanadium [V(IV)] serving as electron acceptors. Copper, gold, and silver did not function as terminal electron acceptors and actually inhibited background levels of lactate oxidation.

Evidence from experiments designed to monitor chromate reduction directly suggest that iron-reducing bacteria effectively reduce Cr(VI) to Cr(III) under anaerobic conditions. Since Cr(III) forms insoluble hydroxides at circumneutral pH and is less toxic than its soluble oxidized counterpart, this metabolism may be an effective means for removing chromate from contaminated waste waters and for determining its fate in natural anaerobic environments.

In FY 1992, we focused on the enzymatic transformation of the cobalt ethylenediamine-tetraacetic acid (Co-EDTA), a contaminant mixture unique to DOE sites. The synthetic chelate EDTA forms water-soluble complexes with many radionuclide and heavy metal cations. For this reason it is commonly used as a decontaminating agent in many nuclear industries and for processing nuclear materials. The co-disposal of radionuclides, metals, and EDTA profoundly altered the geochemistry of natural systems and, in some cases, resulted in the far field migration of inorganic contaminants and radionuclides, including radioactive cobalt ($^{60}$Co). Co(III)-EDTA is a highly stable complex (Log K = 41) that weakly adsorbs to negatively charged particulates such as aluminum oxides at neutral pH. In comparison, reduced cobalt complexed by EDTA [Co(II)-EDTA] is much less stable (Log K = 17) and absorbs to a greater extent. The reduction of EDTA complexes $^{60}$Co(III) to $^{60}$Co(II) should reduce the mobility of this radionuclide in the environment.

Three different iron-reducing bacteria enzymatically reduced Co(III)-EDTA to Co(II)-EDTA under anaerobic conditions. The reduction of Co(III)-EDTA occurred only in the presence of active cells and an appropriate electron donor. Co(III)-EDTA reduction was not observed in tubes which contained heat-killed cells or in tubes which lacked an electron donor. Cell growth correlated with Co(III)-EDTA reduction and ceased when all the Co(III)-EDTA had been reduced. These results expand the range of known suitable electron acceptors for anaerobic growth to include a complex known only to exist through human activity [i.e., Co(III)-EDTA]. Moreover, this metabolism might influence the fate of $^{60}$Co in contaminated subsurface environments at DOE sites. We hypothesize that microbial reduction of Co(III)-EDTA will retard $^{60}$Co migration in environments predominated by iron-reducing bacteria. An invention report was filed on this novel microbial reduction process.

We intend to expand our experimental system to include the pertechnetate anion ($^{99m}$TcO$_4^-$), which is mobile at DOE sites. We will investigate microbial induced reduction of pertechnetate [Tc(VII)] to the reduced less mobile Tc(IV). The overall goal of this work is to understand the mechanisms of inorganic contaminant reduction to allow us to suggest remediation strategies to aid in the cleanup of contaminated DOE sites.
Publications

Two abstracts are currently being written for submission to peer-review journals:


Epidemiological Study to Examine the Relationship Between UV-B Induced Immunosuppression and Infectious Diseases in Humans

J. D. Longstreth (Technology Management Planning)

One of the unanswered questions regarding a potential health effect of stratospheric ozone depletion is whether the immunosuppressive effects of UV-B observed in humans and animals have an effect on the progress of infectious disease in a human population. This project was designed to gather preliminary information on this question in order to determine whether it makes sense to propose a full-scale infectious diseases epidemiologic study of the subject.

In order to explore the potential relationship between UV-B exposure and the incidence and/or severity of infectious diseases, a location was sought with widespread problems with infectious diseases and large natural variations in UV-B. Preliminary investigations indicated that the island of Madagascar met these two criteria; it has a latitude gradient of approximately 10 degrees, and malaria, plague and several other infectious diseases are endemic. In addition, a highly respected tropical disease research organization, the Institute Pasteur, has had a presence on the island for many years and has gathered information on these diseases, some of which has been published. During FY 1992, literature which could be accessed in the public domain was gathered and two estimates of UV-B exposures were developed using information from a National Aeronautics and Space Administration (NASA) satellite model in one case, and information from the National Center for Climate Research as the other. Data on infectious diseases, including several studies exploring the geographic distribution of diseases across the island, were retrieved. Virtually all such information was in French; following translation the data have been entered into a database with the intent of exploring correlations between the UV-B exposure estimates. At the same time, a number of unsuccessful attempts were made to open communication with the Institute Pasteur on Madagascar.
Fundamental Research in Subsurface Environmental Science

R. E. Wildung (Laboratory Programs)

This project was focused on developing an understanding of fundamental chemical, biological, and physical processes needed for an expanded basic research program to understand natural subsurface systems. The project is providing the basis for resolution of problems in prediction and remediation that are critical to DOE's environmental restoration mission. Project activities involving staff and resources at PNL and universities nationwide provide a starting point for developing the interdisciplinary teams and facilities needed to address complex environmental phenomena that occur from the molecular to the field scale. Fundamental areas under development included chemical desorption/dissolution kinetics in aqueous systems, enzymatic transformations and enzyme redesign, and experimental and computational concepts for coupling and scaling molecular-level phenomena to predict system-level response to manipulation for restoration.

Subsurface chemical, microbial, and physical processes governing contaminant behavior and the efficacy of in situ remediation operate simultaneously and interactively. This project is focused on developing new theoretical, experimental, and computational concepts for describing how these processes are coupled and scaled in natural subsurface environments. To properly direct the research, a conceptual model of the linkages between fundamental processes in the subsurface was developed. A framework was then superimposed on the process models to identify the appropriate scales and where these linkages occur. From this exercise, principal research needs were identified and experimental approaches devised using a multidisciplinary team of scientists.

New laboratory experimental approaches were developed for examining the kinetics of mineral/solution interactions (sorption/desorption processes), and microbial-chemical interactions (microbial degradation of organic complexing ligands, microbial transformation of chemical oxidation state). To apply this knowledge in complex subsurface systems, new concepts, capability, and intermediate/field-scale approaches were developed for describing the relationships between linked chemical/microbial processes and heterogeneity in subsurface microbial, chemical, and physical properties.

Research on sorption/desorption was facilitated by development of a close linkage with the University of Delaware to successfully apply pressure jump techniques in conjunction with advanced spectroscopy for measurement of sorption/desorption kinetics. Interfaces were also developed between the Earth and Environmental Sciences (EESC) and the Materials and Chemical Sciences Centers (M&CSC) to apply electron spin resonance spectroscopy to the examination of mineral surface chemistry as a basis for determining the effects of chemical changes on these equilibria. Interfaces were also established between the EESC and the MSRC to successfully demonstrate the use of molecular-level measurements for quantitating chemical reactions on mineral surfaces in natural subsurface environments.

Examination of the enzymatic reduction of uranium and chromium required recruiting of a postdoctoral candidate from the U.S. Geological Survey. Close supervision of the research in concert with the development of new concepts for experimentation allowed the methodologies to be focused on elements of concern to DOE and Hanford, i.e., U, Cr, and cobalt in a complexed state. Each were shown to be enzymatically reduced. New capabilities developed on a companion project will allow the isolation, purification, and cloning of representative enzymes for possible incorporation in natural microbial populations. This would allow both in situ and surface treatment of these elements--as chemical reduction in all cases would markedly reduce mobility in groundwaters or serve as a concentrating mechanism in surface treatment. Furthermore, a detailed assessment of the contribution of the radionuclide technetium in dose calculations for select DOE sites suggested that this element should receive additional emphasis in future studies of radionuclide behavior in the subsurface.

The importance of technetium results from the high water solubility and biological availability of the oxidized state--pertechnetate [Tc(VII)] which appears
to substitute for the nutrients phosphate, nitrate, and sulfate and be actively accumulated by certain plants and algae. If microbial reduction of this element could be achieved in groundwater, either in situ or after treatment on the surface, major reductions in estimated dose to human population could be achieved. Little is known of the ability of microorganisms to accumulate or alter the technetium oxidation state to more reduced [Tc(IV)] forms such as oxides and sulfides, which could be markedly less soluble.

It was concluded that two exploratory efforts were needed to establish the feasibility of biologically altering technetium form/mobility in nature— as a basis for future research proposals. First, it is critical to examine the ability of microflora to accumulate the element as observed for higher organisms to determine if active growth and concentration could be used to decrease solution concentration of the element. Second, it will be necessary to determine if microbial-induced reduction could occur. Earlier (unpublished) studies included growth of bacteria (24) and fungi (12), isolated originally from soil in nutrient media containing technetium or pertechnetate and a series of companion experiments to determine the level of technetium accumulation as a function of prior sulfate induction and competition by sulfate, phosphate, molybdate, chloride, and nitrate— in the presence and absence of active cellular transport inhibitors. A detailed interpretation of the results of this study suggest that pertechnetate uptake by microorganisms does not exceed 30%, but that increases in uptake of 20 to 1100-fold occur when the cells were preconditioned by growth in sulfur-free media, although sulfate did not inhibit technetium transport by sulfur-starved organisms.

Inhibition was not observed with the anions, phosphate, molybdate, chloride, or nitrate. Pertechnetate transport followed saturation kinetics with a $K_m$ of 50 $\mu$M and was pH-dependent with maximal observed activity of pH 3.0. Inhibition was observed with 2,4-dinitrophenol whereas azide enhanced pertechnetate uptake, approximately twofold. Inhibition of uptake by 2,4-dinitrophenol appeared to occur because of enhanced export of pertechnetate from the cells in the presence of the inhibitor. The exact mechanism of azide enhancement is not known, but azide did not alter the chemical form. Pertechnetate and sulfate do not appear to share the same transport mechanisms with Trichoderma-380, although methods that induce sulfate transport also induce pertechnetate transport.

Future studies will focus on uptake mechanisms and reduction processes with organisms known to reduce iron and other elements.

Chemical equilibrium and microbial reduction phenomena must be placed in the perspective of other processes occurring concurrently, if the results are to be successfully applied in natural subsurface systems. The principal problems arise from the occurrence of these phenomena during water flow (and the dynamics associated with continuous changes in chemical composition of the water) and by heterogeneity of geologic processes (e.g., layering and sorting of sediments, mineral inclusions, diagenesis) which, in turn, influence microbial distribution and function and chemical relationships.

To address the problems of quantifying chemical and microbial processes during water flow, this project is developing an overall scientific approach for selectively introducing physical and chemical heterogeneity into experiments at the intermediate (meter) scale. This approach has served as the basis for development of DOE proposals for long-term study of these phenomena in the laboratory and field. Future efforts will validate initial hypotheses and approaches through systematic intermediate-scale investigation of natural mineral stringers and inclusions incorporated into well-sorted sands to simulate natural subsurface systems. This configuration will create coupled microbial-chemical reactions measurable in highly controlled flow regimes. The results will provide the basis for integrated models, which will be validated in highly controlled field experiments and used to understand how the subsurface operates as a system and responds to manipulation.

To address heterogeneity issues, a team with unique multidisciplinary background was assembled. This entailed recruiting a highly specialized hydrologic modeler and a geostatistician with experience in subsurface processes and redirecting existing staff with capability in sedimentary morphology, microbiology, chemistry, flow dynamics, and computer modeling visualization. This multidisciplinary team then formed a cohesive unit to develop concepts for examining natural phenomena in heterogeneous media. The result provided a basis for a proposal to DOE/U.S. Department of Defense (DOD/SERDP) to develop detailed information on important phenomena at an intensively sampled (highly characterized) site with observations from the centimeter (microbiology)
to the meter (sedimentology) scales. The proposal built on and incorporated new sampling, scaling, and field manipulation (e.g., addition of water) approaches developed on this project to extrapolate to larger (10- to 100-meter site, and regional) scales.

Publications


Genetic Profiling of Subsurface Microorganisms

G. L. Stiegler (Biology and Chemistry)

The objective of this project was to develop an easily accomplished direct assay for profiling a possibly complex array of subsurface microorganisms that are deemed important to the bioremediation of DOE sites. Molecular biological techniques are being developed to characterize and distinguish individual microbial populations in subsurface systems.

The methods employed in these investigations were based on direct DNA sequence analysis of variable regions in the 16S ribosomal RNA gene. The assays used the highly conserved (across species) rRNA nucleotide sequence for designing universal polymerase chain reaction (PCR) primers. The primers were positioned to amplify across rRNA gene regions that showed maximum variability between species. The analysis of the amplified gene products were accomplished by cloning and nucleotide sequence determination. It is believed that the nucleotide sequence information that is obtained from these data will provide a means of microbe identification based on synthetic species-specific DNA probes.

Our first year of work has accomplished the following:

- We have designed and synthesized PCR analysis primers that enable us to amplify and analyze approximately 75% of the 16S rRNA gene. The PCR primers were chosen for their nucleotide sequence conservation across species so they would be non-selective in species amplification specificity accommodating an essential design criteria. We have empirically shown that the primers amplify unique 16S rRNA gene regions without apparent bias for sequence.

- We have applied a system using nested PCR primers for obtaining molecular clones of amplified variable gene regions. DNA sequence analysis of cloned 16S variable gene regions from mixed microbial population samples has been obtained using an automated DNA sequencer. We have compiled the DNA sequence information into a database.

- We are using the database information for designing species-specific DNA probes and developing microbial identification methods based on the single-strand conformational polymorphism assay (SSCP). Our probe development will emphasize specificity, rapidity of use, and potential patentable methods of automated analysis based on probe specificity.
Global Environmental Decision Making

J. A. Edmonds and S. R. Rayner (Technology Management Planning)

The goal of this project is to analyze the role of governmental and nongovernmental decision making in the processes that lead to global environmental change as well as in responding to change. Thus initial emphasis is on construction of a conceptual model that identifies critical decision points and the interactions required among various fields of study that would be necessary to trace the effects of decisions across diverse organizational and geographical scales. This was done first for global land-use change. This model is being modified for energy and industrial decision making. The next steps will be empirical research into the role and characteristics of private-sector decision making as defined by the model.

The purpose of this study is to define an interdisciplinary problem area, specify essential information inputs for analysis, and perform pilot studies related to the role of governmental and nongovernmental decision making in the process leading to climate and other global environmental changes, as well as in determining human responses to such change. This work will provide a framework for the future construction of specific computer simulation models and for the design and conduct of policy implementation evaluations.

Because a variety of leading bodies (including the International Geosphere-Biosphere Program, National Research Council, and the International Social Science Research Council) have recognized land use as a critical factor mediating between socioeconomic behavior and global change, we chose land use as the focus of the first phase of this project. Our approach was inspired by a working group discussion at the 1991 Summer Institute of the Office of Integrated Earth Studies at UCAR (University Consortium for Atmospheric Research). This distinguished interdisciplinary group called for development of a wiring diagram or conceptual model for studying the role of human decision making about land use in global environmental change. Thus, the first task of this LDRD project was to develop such a model to identify critical information flows, decision points, and the interactions among various fields of study that would be necessary to trace the effects of decisions across diverse organizational and geographical scales.

The development of the conceptual model was achieved through a thorough review of the relevant literature on land use, decision making, and environmental change; by expert elicitation through telephone and personal interviews with leading authorities in relevant fields; and through qualitative analysis of this information. The model identifies a diverse set of social science and natural science disciplines as providing critical information inputs to any comprehensive analysis of land-use change and its global environmental consequences. The model encompasses individual human aspirations, consumption-production decisions at the level of plot managers, national decision contexts, and the international political economy. The relationships of these factors to population, local land assessments, regional meteorology and air chemistry models, and global climate change assessments are also mapped and described.

The description accompanying the model postulates that the effects of land-use practices on the environment and the impacts of environmental change upon human societies is best analyzed by examining the production systems and management initiatives at the local level for a set of commodities that involve use of land as a resource. This involves tracing the demand for these commodities (and the ability to meet that demand by various strategies) back to human aspirations. It also involves tracing the effects of production forward through the modification of land cover, nutrient cycling, soil quality, and the emission of trace gases aggregated into global processes, manifest as regional changes in physical climate and potential ecosystem productivity.

An important conclusion from this investigation is that the extent, technology, and intensity of the associated production and resource management systems are the primary linking variables between the natural science and social science aspects of global change. Land use and land cover become derived aggregations, useful as
summaries that may be compared with available data, but not fundamental to the linkage process as is conventionally assumed.

This phase of the research has advanced the state of the art in understanding the relationship of human decision making and global land-use change in the following ways:

- We have identified a structure for research that combines social science decision making perspectives with the materials flows systems approach of natural scientists to create an integrated perspective on land-use change that is evenly comprehensive across the social and natural science issues.

- It is fairly transparent and thus able to be assessed for the feasibility of operationalizing the linkages.

- It is designed for modular elaboration of its components, which facilitates identification of relevant research communities not currently involved in global change research. It also will encourage them to enter the field where their skills and information are critically needed.

- Information flows are tightly linked so that research communities specializing in one or another module can now identify the informational needs and offerings of other specializations at the linkage points among the modules.

- It provides the framework for a research program to build an analytic capability for remotely sensed data on land/use cover change that can relate cover changes, trace gas fluxes, and other environmental phenomena to human activities at local, regional, and national scales of human organization. Such an analytic capability is an essential, but currently missing, component of existing remote-sensing programs.

- It suggests priorities for the kind of data that would be useful for understanding land-use/cover change. This will be essential in sorting the huge data outputs that we anticipate from future remote-sensing programs, as well as non-remote data.
The study of the structure and dynamics of high molecular weight biopolymers by NMR spectroscopy requires the development of higher field superconducting magnets. In turn, this requires the development of high frequency NMR instrumentation capable of performing an ever-increasing number of complicated pulse sequences. The object of this proposal is to design a prototype NMR console capable of performing any of a wide variety of multidimensional NMR experiments as well as a variety of NMR imaging experiments. Specific objectives include the design of a fully programmable and expandable logic pulser, a high speed data acquisition system, a radiofrequency receiver, a radiofrequency transmitter, a programmable current pulser, and a radiofrequency pulse shaper. New NMR instrumentation will be coupled to a program to develop and evaluate NMR techniques for applications in environmental problems, including effects of pollutants on DNA structure.

Research on spectrometer design has led to conceptualizations of various pulse programmer (PP) architectures. These architectures include sequential state machines and two FIFO-driver architectures. The sequential state architecture has been successfully applied to three spectrometers at the University of Washington. The architecture has the advantage of being very fast in the execution of pulse sequences, but suffers from a restrictive structure. FIFO-driven architectures were introduced almost 20 years ago, but at that time suffered from small memory size and slowness in the input loading speed. The latter limitation required the introduction of an input buffering microprocessor which necessitated additional program development. None of these limitations exist today, so the FIFO-driven architecture, in some form, is recommended. We conceive of a system in which a UNIX workstation directly loads the PP. We further propose that the PP programming is based on the C language and that pulse program commands (e.g., pulses, delays) be C language subroutines. This strategy will remove the need for writing custom PP language compilers or interpreters. An INDIGO workstation has been procured for the purpose of developing software for the pulse programmer. Efforts for the immediate future involve conceptualization of Digital Acquisition Processor (DAP) structures, followed by radiofrequency system design.

DNA structural research activities with Dr. Michael Kennedy, an Alexander Hollander postdoctoral fellow, were centered around investigation of slow molecular dynamics at the TpA cleavage site in the T3A3-containing AhA III and Pme I restriction sequences. We have observed that the adenine H2 and H8 proton lines, which reside in the minor and major grooves respectively, are broadened due to motion. In analogous A3T3-containing sequences, adenine H2 and H8 resonances are of normal linewidth. Assuming chemical exchange in the form of conformational dynamics (e.g., oscillation of the purine base about the glycosidic bond), spin-locking relaxation data and 2D NOESY were used to constrain the correlation time of the internal motion to a range between the T1 and T1 rho minima. Calculated lineshapes using a two-site model indicate that the motion has an amplitude of 20 to 50 degrees with an associated correlation time of 160 μsec/rad to 10 μsec/rad. The mobility appears to be a result of the structure at the TpA junction which is characterized by a narrow minor groove, an unusual average conformation of the adenine heterocycle resulting from poor base-stacking, and a sharp discontinuity in the sugar conformation at the TpA step.
High Performance Computing

T. H. Dunning (Theory, Modeling and Simulation)

This project was intended to advance the state-of-the-art in using high performance, parallel computing technology. More specifically, the focus was on developing the ability to solve, using parallel computing technology and techniques, new classes of environmental transport and engineering problems currently intractable with standard computing equipment.

Elliptic partial differential equations are ubiquitous in mathematical descriptions of physical phenomena. Equations of this type appear as the pressure equation in the incompressible Navier-Stokes equation for simulating fluid flow, in the Poisson and Helmholtz equations for simulating electro-static fields, and in the concentration equations of different liquids in porous media flow. Since the solution of the elliptic equation propagates infinitely fast across the physical domain, current serial methods cannot be made to run in parallel without incurring significant waiting and communication time. Thus, new parallel algorithms must be developed which are accurate but with less communication cost. Since our intended goal is to produce a robust solver for the general purpose CFD code TEMPEST, the new algorithm must also be adaptable to a variety of parallel computer architectures.

We have developed and implemented a two-level, domain decomposition-Schwarz method with small overlaps for solving elliptic partial differential equations assuming a message passing model for parallel computation on MIMD computers. A multi-color scheme for communication and for the Schwarz alternating solve was also implemented. In addition, an SOR scheme was incorporated on the overlapped region to accelerate convergence for the Schwarz solve. The elliptic solver and the communication codes were incorporated into the TEMPEST version T CFD code for the CCSF's Touchstone Delta and the Intel iPSC/860. On a small test problem with 5100 unknowns we were able to achieve a speed up of two on four processors using an unoptimized test code. Increasing the number of processors yielded poorer results--due to small problem size, load imbalance, and communication overhead. However, we noticed that the completion time is almost independent of problem size/processor numbers. If we optimize the code, we may be able to solve much larger problems on more processors in the same amount of time as a smaller problem on one processor.

Currently, we are developing a coarse domain to fine domain projection method and a fine to coarse approximation method with a GMRES preconditioner for accelerating global convergence. We are also porting the TEMPEST to a cluster of IBM RS6000 super-scalar-workstations with the intent of using it for production simulations.
Improved Radionuclide Characterization

H. S. Miley (Nuclear Chemistry)

The purpose of this project is to demonstrate high sensitivity measurement of radioactive isotopes using unique detection technology. Major improvements in sample analysis may be achieved in a high visibility detection system, which could integrate low-background technology with new, large volume, segmented detectors and specialized acquisition/analysis software. Segmented low-background detection systems can electronically separate/identify isotopes by their decay scheme, reducing or eliminating radiochemistry in sample preparation. A high efficiency segmented system would also be able to analyze low mass high-level samples, thus contributing to assay of various waste materials without requiring large sample preparation, storage, or disposal efforts.

Radioisotope ID, and in particular gamma-ray spectroscopy, has been an invaluable aid in basic scientific understanding, and has also played a significant role in laboratory research in support of many industrial processes, U.S. government applications, waste cleanup, and many other activities. However, as always with scientific technologies, a static technology is always overtaken. This is the case with ordinary radioisotope ID. Competing technologies, such as mass spectrometry, have supplanted a large portion of the business previously allotted to gamma-ray spectroscopy.

However, there are still significant advantages to certain applications of gamma-ray spectroscopy. One possibility, not used in standard radioisotope ID, is high efficiency segmented detectors. This is simply using several detectors in tandem to do a better job than one alone could do. However, the improvement factor is significantly better than the increase in detector mass or simply the increase in number of detectors. That is, two detectors are far better than twice as good. The basic concept utilized here is that decaying radioisotopes have distinct signatures which may affect a pair of cooperating detectors differently than one single detector. This allows greater segregation of signals and thus, improved detection of small signals in the presence of large signals.

Operating gamma-ray detectors in coincidence is not new technology. However, advanced handling of the signals obtained is new technology. Typically, systems have been designed using modular electronic systems to handle two gamma rays of specific energies. This is useful for searching for one specific isotope, but requires considerable high-level effort to calibrate and adjust for any second isotope. Some systems have allowed for a true two-dimensional signal, but these usually have been low resolution devices.

Our approach has been to investigate n-dimensional data, where n is the number of detector segments and is not fundamentally constrained. Actual laboratory work has been with n equal to 2, 3, 4, and set-up work for 6. The laboratory work has educated us on several technical constraints. First is the speed of acquisition. Multiple detectors yield lots of signal; our remedy is to use a fast system and to use fast electronic hardware to deselect large amounts of uninteresting data. The second problem is "accidentals." Accidentals occur when two gamma-rays of unrelated origins are recorded in detector segments within an electronically defined "resolving period." The solution to this problem is tight timing characteristics for all electronic components.

In order to address the problems above, we undertook to develop in-house electronic hardware to process signals and make selection/deselection decisions very rapidly. This has resulted in a prototype version of a highly dense, highly parallel, extremely versatile trigger circuit. This novel circuit has already drawn the attention of several researchers for completely different applications. Review of commercial circuits has shown no similar system on the market, and to reproduce this system would take as many as two dozen typical modular components or several state-of-the-art modular components.

Laboratory work demonstrated the critical ability to observe exceedingly weak radioisotopes of multiple gamma-ray signature in the presence of very strong signals of lower multiplicity. This was done with slow electronics, a crude commercially supplied trigger circuit and (in hindsight) sloppy timing. The new
electronic circuit has been designed to reduce accidentals, our limiting factor in early work, by a factor of about eight.

An interesting sidelight on the laboratory work was much deeper understanding of the gamma-ray/detector interaction, particularly the Compton effect. Our laboratory results showed a substantial amount of signals in one detector correlated to another such that the sum interaction energy was the energy of one of the gamma-rays of interest. This is the rather unlikely outcome of a gamma-ray initially interacting in one detector (via the Compton effect), leaving a small energy deposit, then proceeding to another relatively remote detector to deposit the balance of its energy. This two-detector, one-gamma-ray effect has been used as the basis of a significant proposal to the Underground Storage Tank Integrated Demo (UST-ID).

This project has been so successful that it is recommended that additional support be provided to continue the development of the n = 6 detector set-up.
Infrared Atmospheric Continuum Absorption

S. W. Sharpe (Chemical Structure and Dynamics)

Isolated clusters of $\text{H}_2\text{O}-\text{Ar}$ and $\text{N}_2\text{O}-\text{Ar}$ were produced by a novel pulsed slit supersonic expansion and studied in the 2000 and 1600 cm$^{-1}$ spectral regions via a high resolution infrared diode-laser. We have developed accurate models to explain the observed results for the $\text{Ar}-\text{N}_2\text{O}$ dimer and are in the progress of analyzing the $\text{H}_2\text{O}-\text{Ar}$ dimer. These preliminary studies are necessary steps in gaining an understanding of and optimizing the instrumentation. Research has now begun on the water complexes.

The development of a direct absorption, high resolution, infrared experimental capability at PNL is complete. The apparatus has allowed us to create a large assortment of small clusters (e.g., $\text{N}_2\text{O}-\text{Ar}$, $\text{N}_2\text{O}-\text{CO}_2$, $\text{N}_2\text{O}-\text{CO}$, $\text{H}_2\text{O}-\text{Ar}$ ...) and probe these clusters via a tunable infrared diode laser. In addition, the applicability of this instrument is not limited to clusters but may be used to simplify the spectra of all volatile, infrared active molecules. Present capabilities include the infrared region from 2400 down to 600 wavenumbers. A brief description of both the technique and instrumentation will be given.

Many of the problems that plague conventional spectroscopic techniques have been avoided by creating and examining molecules and weakly bonded clusters in a collision free environment. In these experiments, a samples is entrained in a high pressure carrier gas. The carrier-sample mixture is allowed to expand into a high vacuum chamber. During the expansion, molecules are cooled adiabatically, and undergo complexation. Typical rotational temperatures in these types of experiments are 1-2 K. The clusters are then probed using a diode laser technique pioneered by this author. 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 clusters into their lowest rotvibrational states while the unique nature of a slit expansion removes most of the Doppler broadening inherent in standard spectroscopic techniques. Both of these effects work in concert to increase the sensitivity of this infrared absorption technique. Through the judicious choice of infrared diode lasers, all infrared active molecules can be studied.

The Pacific Northwest Laboratory’s infrared-diode-laser spectrometer is similar in design to those of DePliante et al. (1989) and Sharpe et al. (1990) and takes advantage of the fast tuning ability of diode lasers. Several changes and refinements have been made resulting in a significant improvement in sensitivity. A stock diode-laser system (Laser Photonics) was modified by removing the closed-cycle cold head from the supplied enclosure and securely tying it to the optics table. This reduced acoustic vibrations within the cold head and mechanically decoupled the cold head from the collimating optics. Once collimated, the laser radiation is directed into a 0.5-meter monochromator to achieve mode selection. The output of the monochromator is then intercepted by a rotating, gold coated aluminum sector. The sector mirror is mounted on a stepper motor and depending on the angular position of the sector, light will either pass through or be reflected. In its present configuration, the sector intercepts and directs the laser light 1/3 of the time to a reference cell and 1/3 of the time to a 0.25 meter confocal étalon. For the remaining time, the light is transmitted straight through and brought into the vacuum chamber where it intersects the effluent of a pulsed, slit nozzle. By steering the laser radiation sequentially in time we are able to direct the full beam of light to the jet, reference and étalon. In addition, we avoid having to stock and change an assortment of beam splitters when switching spectral regions. Light from the jet, reference and étalon are all brought back to a single infrared detector. Laser light entering the vacuum system is multi-passed up to 32 times through the supersonic jet by utilizing a standard White-cell optical configuration.

The vacuum system consists of three regions: an expansion, a differential and a quadrupole mass spectrometer chamber. A closed-cycle freon cryobaffle ($-120^\circ$C) is used to trap a 20" diffusion pump and maintains the expansion chamber at $10^{-7}$ Torr when no load is present. The cryobaffle is required to prevent
back-streaming of the diffusion pump oil onto the White-cell optics. A 1.0 mm conical skimmer separates the expansion and differential chambers, while a 5 mm orifice separates the differential and mass spectrometer chambers. The last two chambers are evacuated with individual stacks which include a 6" diffusion pump, an LN2 trap and a gate valve. Only the expansion chamber sees a significant gas load and is generally operated slightly below the maximum pumping capacity. Average pressures during valve operation are 5 \times 10^{-4}, 5 \times 10^{-5} and 2 \times 10^{-7} Torr for the expansion, differential and mass spectrometer chambers, respectively.

Three solenoids (General Valve) are operated in parallel and pull a Viton sealing surface from a 12 cm x 200 micron slit. The slit is cut into an aluminum plate using a jewelers’ slitting saw. Mass spectrometer traces corresponding to 40 amu (argon) indicate a 2 millisecond pulse of gas with a sharp onset and an exponential tail. For experiments involving Ar-N2O dimers we found that a mixture of 1% N2O in UHP argon at a backing pressure of 600 Torr gives optimum signal, while higher pressures actually decrease the infrared signal. Based on an expansion chamber pressure of 5 \times 10^{-4} Torr and a pumping speed of 9,000 liter\textpersecond\meter, the nozzle throughput is calculated to be 4.5 Torr\textpersecond\meter at a repetition rate of 3 Hz. It should be noted that this is an apparent throughput based on a duty factor of 0.006. If the valve were operated in a continuous mode, the actual throughput would be about 750 Torr\textpersecond\meter!

Depending on the specific diode and its tuning characteristics, it is possible to scan up to a 3-cm\textsuperscript{-1} spectral region; but we typically ramp 0.5 cm\textsuperscript{-1} to maintain spectral resolution. Signal averaging is accomplished by the real-time co-addition of individual spectra over many gas pulses. Ultimately, laser drift will broaden spectral signals and limits us to about 1,000 averages at a 3-Hz repetition rate. When spectral averaging is kept under 250 co-additions, instrumental line widths are usually below 20 MHz (FWHM).

References


Publications

"Infrared, Diode Laser Spectroscopy of the Ar-N2O Complex: Observation of the Intermolecular Bending Mode in Combination with the Highest Frequency Intramolecular Stretching Mode." Journal of Chemical Physics (to be submitted).


"The Infrared Spectroscopy of the Nitrous Oxide Dimer in the 2,220 Wavenumber Region." Journal of Chemical Physics (to be submitted).

"The Infrared Spectroscopy of the CO-N2O Complex in the 2,220 Wavenumber." Journal of Chemical Physics (to be submitted).

"The Infrared Spectroscopy of the CO₂-N2O Complex in the 2,220 Wavenumber." Journal of Chemical Physics (to be submitted).
Diode Laser Spectrometer
Integrated Regional Climate Change

W. T. Pennell (Atmospheric Sciences)

This research had three major objectives: initiate development and testing of methods for translating the coarse resolution predictions of global climate models (GCMs) to the finer scale resolution required for impact assessment studies; continue development and testing of a model for assessing the impact of potential climate change on regional-scale surface hydrology and water resources; and compile and analyze regional-scale paleoclimate data for the purpose of understanding the linkages between global-scale and regional-scale climate change and for testing the regional-scale climate modeling methodologies developed under the first objective.

During FY 1992, a regional circulation model (MM4) was obtained from the National Center for Atmospheric Research. Appropriate climate physics (solar radiation, infrared radiation, cloud microphysics, and surface physics) were added to adapt the model for climate applications. The spatial resolution of the surface boundary conditions in the nested domain was improved by using surface elevation resolved by the fine nested grid rather than interpolated from the coarse outer mesh. A known climate bias was removed by treating horizontal diffusion on constant pressure surfaces rather than on terrain-following surfaces. Lateral boundary conditions from a global climate model simulation and from observations were obtained. Appropriate output variables for driving surface hydrology and ecology models were identified and added to the model history fields. The model code, which was developed on CRAY supercomputers, was adapted to run on RISC UNIX workstations by introducing substitutes for CRAY vector functions and eliminating dynamic memory allocation. Timing tests were performed on two different machines and a workstation was purchased and installed. Meteorological station data for the Pacific Northwest were obtained for verification of the simulated climate, and preliminary simulations were performed.

The efforts in hydrology during FY 1992 focused on improving the treatment of evapotranspiration (ET) in watershed models. This process is typically the model component with the least physical realism. Two influences, in particular, were incorporated in a new state-of-the-art spatially-distributed physically-based watershed model, PNL-WATERSHED: 1) the effect of water table position and its fluctuations on evaporation and transpiration, and 2) simulating the way vegetation controls the rate of transpiration under various climate conditions. As the first step in developing an improved ET module, the influence of fluctuations in solar radiation and temperature on daily mean ET rates was investigated. The investigations were then extended to other effects. The ET parameterization is sufficiently detailed to treat the effects of a variety of forcing factors, such as changes in temperature, rainfall, cloud cover, irradiance, soil water potential, etc. The parameterization scheme was tested using data from the Middle Fork Flathead Watershed in Montana. A technical discussion of selected aspects of the model are presently under external peer review.

In paleoclimatology, data is required both as boundary conditions for driving the climate model and as verification of the climate simulation. During FY 1992, the pre-existing paleoclimate data for year 7000 B.P. in the Pacific Northwest was compiled for a wide range of proxy indicators. Key areas requiring additional research were then identified.

Publications


Integration of Molecular Research with Environmental Phenomena

R. E. Wildung (Laboratory Programs)

The objective of this project is to perform research in organic geochemistry and in microbial physiology and biochemistry through joint appointments at Washington State University that will link molecular-scale investigations in chemistry and microbiology to processes occurring in the environment as a basis for solution of problems in environmental restoration.

New and innovative approaches are required to perform research directed toward the successful restoration of contaminated environments. To address these needs, joint efforts were undertaken with WSU Tri-Cities to develop new research in critical scientific areas. Research is being conducted in PNL facilities. The approach involves investigating key linkages between molecular-level phenomena and the manifestations of these phenomena in the environment. Thus, a capability in enzymology is being developed as a link between mathematical models of enzyme structure and function and biodegradation processes actually occurring in the field. Similarly, the capability to investigate interactions of contaminants with natural surfaces links studies of bonding mechanisms with geochemical reactions controlling sorption/desorption and aqueous transport of organic/radionuclide mixtures in the environment.

In FY 1992, a joint PNL-WSU position in microbial physiology (enzymology) was filled and research 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 NTA degradation. In addition, the genes regulating the expansion of these enzymes in subsurface microorganisms were cloned. Research approaches, equipment, and facilities were marshalled and implemented to apply advanced spectrometric methods to elucidate contaminant bonding mechanisms and their role in governing contaminant mobility and remediation effectiveness. Research in organic geochemistry is planned to be initiated in FY 1993.
Kinetic EPR Spectroscopy to Resolve Sorption Mechanisms

J. A. Franz (Chemical Sciences)

This research examined the scope of applicability of electron paramagnetic resonance (EPR) spectroscopy and laser photoacoustic spectroscopy (PAS) to evaluate spectroscopic methods for determination of kinetics and characterization of the reactivity of mineral phases with EPR-detectable ions at the molecular level.

The project was successful in observing, both by EPR and PAS, the kinetics of absorption and complexation of organic substrate and copper ions with clay mineral suspensions. This project successfully assembled instrumentation for kinetic EPR spectroscopy and kinetic and static laser photoacoustic spectroscopy. The methods were successfully applied to observing the reaction of an organic substrate, 1-aminonaphthalene (AN), with a clay surface, and with a clay mineral treated with copper ions. The methods enable actual kinetic measurement of intermediate formation, and direct observation of redox metal reactions on a clay surface. With a small amount of additional effort, the studies will result in papers on oxidation kinetics and mechanisms of organic substrates on clay minerals. The methods are potentially important for characterization of soil reactivity.

EPR Spectroscopy

Stopped-flow kinetic EPR instrumentation was assembled. The instrumentation allowed the observation of kinetics of reaction of colloidal suspensions with EPR-detectable ions. Further work has been carried out to apply static and kinetic EPR spectroscopy to detect organic free radicals and EPR-active metal ions on clay surfaces onto which EPR-detectable ions have been absorbed.

Electron paramagnetic resonance spectroscopic analyses were performed to determine the applicability of this technique for monitoring the kinetics of clay substrate reactions. For example, paramagnetic metal ions on or in the clay may become diamagnetic on reduction by organic substrates. Accordingly, the rate law for oxidation can be obtained from the time-dependence of the EPR signal. Also, if paramagnetic intermediates are formed from the organic substrate, then they may be observable by EPR and provide additional kinetic information. Aminonaphthalene was used as the organic substrate in these studies because it is reported by PNL investigators to react with the iron-containing clays generating iron colored and polymerized products. Unfortunately, no useful EPR signals could be observed from nontronite or from mixtures of nontronite and aminonaphthalene (ANP). The absence of detectable carbon-centered radicals demonstrated that, contrary to previous studies based on the evolution of colored complexes during AN oxidation, no persistent radical cations of the substrate are formed on montmorillonite.

Whereas Fe(III) ions are difficult to observe, Cu(II) ions are readily observable by EPR. We were able to observe the EPR signal of Cu(II) adsorbed to hectorite clay suspended in water. The spectrum is indistinguishable from that for Cu(II) ions in water.

Reactions of Cu(II) with ANP were investigated in homogeneous solution in order to determine what might be expected to occur when ANP was reacted with Cu(II) on hectorite. Cu(II) ions react very slowly with ANP in water to form a dark blue solution indicative of complexation between Cu(II) and ANP. This complex was observed to form rapidly in solutions of wet acetonitrile. EPR analyses of this complex showed the signal to be essentially the same as that for Cu(II) ions in water. The signal slowly decayed with the concurrent appearance of another persistent EPR signal, possibly that of an organic species [no hyperfine structure was observed, however, the line width was significantly smaller than that for Cu(II) and the g-value was consistent with that of an organic radical]. These observations are consistent with reduction of Cu(II) to diamagnetic Cu(I) via an electron transfer mechanism that generates a radical intermediate that may go on and react with substrate to form a persistent organic radical. Furthermore, these findings suggest that similar reactions of ANP with Cu(II) on hectorite should be amenable to study.
by the EPR technique and that the technique can probably be extended to other EPR detectable paramagnetic metal ions such as vanadium. The PAS kinetic technique compliments the EPR techniques in important ways. In particular, the PAS technique provides information on the rate at which the metal-substrate complex forms, while the EPR technique provides kinetic information on the rate at which the metal is reduced by the substrate. Thus, the combination of these two techniques holds promise to provide a much more comprehensive picture of the interaction of organic substrates with transition metals in and on clays.

Laser Photoacoustic Spectroscopy

Instrumentation for time-resolved and static PAS was built and the methods applied to study the reactions of AN with nontronite and montmorillonite clays. The rate of formation of a complex between AN and nontronite and montmorillonite clays was determined by PAS. Intermediate UV-visible spectra of evolving complexes were obtained. The ability to observe kinetics at concentrations suitable for soil studies reveals the static and kinetic PAS technique to be very useful. The kinetics of appearance of AN-clay complex formation were determined and can be interpreted in terms of Fe(III)/Fe(II) complex formation. Thus, the method has been verified for obtaining molecular-level kinetic data for catalytic oxidation of organic substrates on soil minerals, and the method should have wide applicability to studies of organic pollutant/soil interactions.
Land Use and Agricultural Model of Global Environmental Change

J. F. Clarke (Global Studies Program Office)

The objective of the project is to develop a model of the relationships between regional land use, agriculture, regional economic activity and global environmental change, with emphasis on the roles of international trade, human migration, agricultural and land management practices, technological change, and comparative economic advantage. The model is to improve our understanding of the influence of agriculture and land use on greenhouse gas emissions as well as the interaction between climate, land use, and agriculture at the global level on agriculture and other uses of land and water resources.

To understand global environmental change, it is important to understand the interaction of human economic activities both with climate and with the land base at the regional level, and with trade activity at the global level. Potential effects of climate change affect specific regions, specific sectors, e.g. water resources or agriculture, and the effects of human adaptation to climate through international economic trade.

This demonstration project integrates the essential features of a complex land use/agricultural system at the regional level with international markets in a manner consistent with PNLS Second Generation Model (SGM) of greenhouse gas emissions. A model structure was created to investigate the relative importance of international agricultural trade, population growth, technological change, human migration, agricultural and land management practices, use of land for energy production, and other major long-run interactions of human and global environmental change at the regional and international level.

The objective of the work during FY 1991 was to begin to develop a modeling framework for agriculture and land use that allows for holistic analysis and continuing expansion and to determine the minimum model necessary to answer the major interregional questions on the interaction of agriculture and land use with regional and international economies through trade, migration, and investment. A draft paper was begun on the required structure. Modeling issues included: linking economic behavior to ecologic processes; aggregating products such as grain, which is composed of many different crops; accounting for short-term (substitution, regulations) and long-term (technological change) responses at the regional and interregional level; and implementing investment in manner compatible with the SGM generic cost and production and investment modules. We also began to identify data sources on the world agricultural sector, climate, and land use, including the National Center for Atmospheric Research, National Oceanographic and Atmospheric Administration, the U.S. Department of Commerce, U.S. Department of Agriculture, the World Bank, the International Monetary Fund, World Resources Institute, International Comparison Project (University of Pennsylvania), and United Nations (especially UNEP and WMO). We downloaded several relevant climate and land use data sets through INTERNET.

During FY 1992 we constructed a demonstration Land Use and Agricultural Model (LUAM) for the United States, featuring 10 crop production regions and several row crops. It features modules detailing the interaction of world trade (as captured in world crop prices), climate (as embodied by growing degree-days or monthly average temperatures, seasonal precipitation), available technologies, management practices and trade, and costs of resources as they affect land use in each region and agricultural production functions. We are attempting to integrate soil conditions and evapotranspiration, multi-year crops, and crop rotation practices. We also intend to extend the model outside the U.S. and to integrate the results of plant process models such as EPIC or CERES. We have verified that the model reproduces existing crop production with current climate and practices and reacts appropriately to changes in prices of traded agricultural products, technological change in agriculture, population growth, and institutional change. We have begun drafting an article for a technical journal discussing our techniques and the results of the analysis to date.

Integrated Environmental Research 1.1.50
In designing this demonstration model, we have attempted to remain as compatible as possible with PNL's SGM of greenhouse gas emissions. Thus, LUAM is designed to take market prices for crops and other inputs to production such as labor, capital, and fertilizer produced by market solutions in SGM and use them as inputs to the agricultural production processes modeled in LUAM. LUAM then produces estimates of agricultural output, value of land in agriculture, and amounts of land and other inputs to production used in each region's agricultural sector to solve the world agricultural markets and regional land markets in SGM. We designed the LUAM code so that LUAM and SGM naming conventions and functional types are similar. Thus, when fully operational, SGM can directly incorporate LUAM code with a minimum of adaptation, or else LUAM can be run in tandem with SGM if this is more convenient.

In addition, we have organized much of the state-of-the-art data that we collected in 1991 and 1992 into geographic information system (GIS) data sets to describe the natural climatic and land conditions for agriculture and natural ecosystems around the world. With these GIS data sets we have the capability to quickly develop and produce color maps of country or regional data classifying and comparing the world's vegetative land cover, monthly average temperatures and annual growing degree-days, typical monthly and annual precipitation, annual potential evapotranspiration, soil water-holding capacity, and solar insolation. We have used these data to begin modeling the conditions for climate-induced change in "unmanaged" ecosystems. With these data sets we also have the capability to produce estimates of greenhouse gas emissions from agricultural land and natural ecosystems, by country if desired.
Magnetic Resonance Spectroscopy

H. M. Cho (Macromolecular Structure and Dynamics)

A comprehensive array of magnetic resonance-based technology, including solid- and liquid-state nuclear magnetic resonance (NMR), two-dimensional and multidimensional NMR, electron paramagnetic resonance (EPR), and magnetic resonance imaging (MRI) were researched. The magnetic resonance research to which this project is directed can be divided into two general categories. The first consists of the application of magnetic resonance methods to chemical and materials problems related to PNL's research directives in environmental science. Geological samples and molecular sieve compounds are two classes of systems of special, current concern, and were the subjects of closer study by NMR. Paramagnetic biological macromolecules were also considered as candidates for investigations by magnetic resonance methods, both NMR and EPR. The development of novel techniques and experiments in NMR and EPR and the study of fundamental processes in magnetic resonance spectroscopy comprise the second category of projects that were included within the scope of the magnetic resonance research. A variety of methods will be explored theoretically and experimentally to uncover ways of increasing sensitivity, resolution, and information content of NMR and EPR spectra. In addition, advances in instrumentation, such as SQUID detectors, pulsed electron-nuclear double resonance (ENDOR) probes, and magnetic force microscopes were examined, and if found useful, developed and integrated into PNL spectrometers for analytical purposes.

During FY 1992, the initial phases of this project—the design and construction of variable temperature probes for performing nuclear magnetic resonance (NMR) experiments on proton- and deuterium-containing solids, and the development of theories to account for dynamic and static proton NMR lineshapes in silicates was begun. The major parts of the probes were machined, and are currently being assembled and fitted with radiofrequency electronics. These probes implement novel features which will enable detection of proton NMR signals over wide temperature ranges from solid samples having extremely dilute concentrations of hydrogen atoms (less than 1/100% by weight hydrogen).

Theoretical work was conducted in parallel with this experimental effort in an attempt to interpret anomalous proton lineshapes recently observed in anhydrous silicate minerals. Initial results indicate that silicate minerals formed in anhydrous environments—within the earth’s mantle—incorporate hydrogen pairs in well-defined defect sites in the crystal lattice. Further analysis of the NMR data should provide information on the dynamics, if any, of these hydrogen pairs, and the mode of incorporation of hydrogen in these stoichiometrically anhydrous materials. Insight on the correlations between the physical properties of these minerals and the concentration and chemical form of hydrogen is the object of this investigation.

Related work on proton and carbon-13 NMR of organic molecules adsorbed in zeolites was completed. The results reported in these investigations demonstrate that recently developed NMR experiments in combination with traditional analytical techniques, can reveal the distribution and trajectories of motion of guest molecules in voids of a host crystal. The consequences of these observations for zeolite synthesis and catalysis are currently being studied.

Publications


Materials Surface Chemistry

J. Janata (Materials and Interfaces)

The area of mineral surface chemistry included the investigation of mineral and metal oxides, major components of catalysts, ceramics, glasses, electronic and magnetic devices, and corrosive inhibitive films. Unfortunately, the vast amount of work that has been done in the past to characterize oxide surface chemistry has been performed on powders and is difficult to interpret on an atomic or molecular level. Project goals for FY 1992 are to continue the investigation of calcite and tin oxide surfaces via XPS and LEED intensity analyses. Moreover, new tasks will investigate the interactions of water and organics with single crystal iron oxide, alumina, and titania surfaces.

There were four areas of activity pursued during 1992: 1) mineral and oxide surface chemistry, 2) environment-materials study group and related experimental activities (mineral formation and solution chemistry), 3) surface structure calculations and LEED data analysis, 4) development of new capabilities: approaches to synthesis of model mineral surfaces and catalysis.

Mineral and Oxide Surfaces

A series of LEED intensity voltage (IV) data were collected for the (111) and (110) surfaces of tin oxide. The (110) surface has been the subject of considerable experimental study, but no previous quantitative LEED measurements or experimental determinations of structure have been made. The (111) surface is a natural growth surface much more complex than the (110), but we have shown this surface to be much more stable. The experimental data are being compared to theoretical predictions of surface structure in the process of completing the first detailed determination of the surface structures of a non cubic oxide.

A series of x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), reflection electron energy loss and electron stimulated desorption measurements have been made on single crystal calcite surfaces in vacuum and in aqueous solutions. The two thrusts of activity are obtaining experimental data for comparison with theoretical models and measurements of the effects of metal adsorbates on surface chemistry and dissolution. This activity included one of the first applications of a new AFM that arrived in the laboratory in the spring. These have resulted in three publications and a proposal. This activity involves interactions of MSRC with ESRC staff.

Environment-Materials Study Group

A materials-environment study group has been exploring areas where the interactions that occur at surfaces in solution are common to both materials and environmental sciences. Two activities have been generated by this group: 1) phase nucleation on patterned SAM surfaces, and 2) x-ray adsorption spectroscopy (XAS) measurements of atomic arrangements in solution, during precipitation, and in thin films formed from solution. The first activity was in cooperation with the BES Materials program on Biomimetic Materials that was given a DOE award. Dr. Dave Blanchard made two trips to light sources working with Dr. Farrell Lytle to make a series of XAS measurements at Stanford and Brookhaven.

Surface Structure Calculations and LEED Data Analysis

A close tie between the development of the theory of mineral surfaces and experimental studies has been one of our primary goals. During the past year ab initio density-functional calculations of the electronic properties of bulk calcite were performed. To allow comparison of the theory with experimental data, CPS valence band data and reflection electron energy loss data were collected. A comparison of the photoelectron spectra with the ab initio density of states shows excellent agreement. These ab initio results are now being used to parameterize an empirical tight-binding total energy model for the computation of calcite surface and step reconstructions.

Surface reconstructions for both the SnO$_2$, (111) and (110) surfaces have been predicted by the theory, and the LEED IV data are currently being analyzed. The (110) surface has two possible terminations for the fully relaxed surfaces. The reduced surface lacks the bridging oxygen atoms present at the stoichiometric
surface. Both surfaces exhibit slight relaxations in which the surface oxygen atoms move out from the surface while the surface Sn atoms move in towards the bulk. This rumpling relaxation is characteristic of surfaces whose topology does not allow approximately bond-length conserving motions of the surface atoms. The surface atoms cannot move without significantly distorting their local bonding environment. The energy cost associated with these distortions is simply too great, hence the surfaces rumple slightly.

The (111) surface also has two possible terminations, reduced and stoichiometric. Unlike the (110) surface, however, the (111) surface topology does allow a bond-length conserving (BLC) movement of the surface atoms. Moreover, this motion also serves to reduce the dipole moment perpendicular to the surface. Preliminary tight-binding computations have indicated that the surface will relax along this BLC path. We are currently investigating the extent to which long-range electrostatic interactions affect the computed relaxation by explicitly including these interactions in the tight-binding total-energy model.

Development of New Capabilities: Approaches to Synthesis of Model Mineral Surfaces and Catalysis

New staff were hired to develop two important environmentally related surface areas: synthesis of model mineral surfaces and catalytic destrition of contaminants. The approaches to growth of thin film minerals were examined by literature survey and discussion with experts in epitaxial growth. It has been concluded that both growth of some oxides on conducting substrates and the doping of films on insulating substrates can work. A new capability for catalytic studies was designed and will be completed during FY 1993. A subcontract has been arranged with the University of Washington and Professor Tom Engel in Chemistry to partially support a postdoctoral fellow who is developing an atomic force microscope which has the possibility of operating in vacuum and at low temperatures. The first version of this instrument has been completed and has been tested looking at oxide and mineral surfaces.

Publications


Presentations


Materials Theory and Modeling

J. P. LaFemina (Materials and Interfaces)

The goal of this project is to perform fundamental research to develop the theoretical models necessary for obtaining a detailed microscopic understanding of the surface structure, chemistry, and dynamics of mineral oxide, compound semiconductor, and thin-film polymeric materials. These materials are important in areas as diverse as the transport of groundwater contaminants, the creation of advanced electronic and optoelectronic devices for chemical sensor technologies, and the production of advanced materials. Efforts during FY 1992 were focused on the prediction of the electronic and structural behavior of bulk and surface vibrational properties, and prediction of the electronic and structural properties of adsorbed overlayers on tetrahedrally-coordinated compound semiconductors.

The work in this LDRD project can be subdivided into several areas, the details of which are given below.

Mineral Surface Structure and Chemistry

During the past year ab initio density-functional calculations of the electronic properties of bulk calcite were performed. To allow comparison of the theory with experimental data, XPS valence bond data and reflection electron energy loss data were collected. A comparison was made of the photoelectron spectra with the ab initio density of states and the agreement is excellent. These ab initio results are now being used to parameterize an empirical tight-binding total energy model for the computation of calcite surface and step reconstructions.

The surface structures of the cassiterite, SnO₂, (111) and (110) surfaces are being examined by Auger spectroscopy, low-energy electron-diffraction (LEED) intensity analyses and by tight-binding total-energy computations. Surface reconstructions for both surfaces have been predicted by the theory, and the LEED IV data are currently being analyzed.

The (110) surface has two possible terminations. The reduced surface lacks the bridging oxygen atoms present at the stoichiometric surface. Both surfaces exhibit slight relaxations in which the surface oxygen atoms move out from the surface while the surface Sn atoms move in towards the bulk. This rumpling relaxation is characteristic of surfaces whose topology does not allow approximately bond-length conserving motions of the surface atoms. The surface atoms cannot move without significantly distorting their local bonding environment. The energy cost associated with these distortions is simply too great, hence the surfaces rumple slightly.

The (111) surface also has two possible terminations, reduced and stoichiometric. Unlike the (110) surface, however, the (111) surface topology does allow a bond-length conserving (BLC) movement of the surface atoms. Moreover, this motion also serves to reduce the dipole moment perpendicular to the surface. Preliminary tight-binding computations have indicated that the surface will relax along this BLC path. We are currently investigating the extent to which long-range electrostatic interactions affect the computed relaxation by explicitly including these interactions in the tight-binding total-energy model.

Finally, some theoretical work has been done in an effort to characterize the nature of the interatomic repulsions in these materials and the importance of including distant-neighbor interactions into models of surface structure and chemistry.

Structural and Photophysical Properties of Polymers

Our recent work in this area examined a series of isoelectronic substituted polyimides where the structure of the polymer backbone was determined by quantum-mechanical AM1 geometry optimization, and the photophysical properties computing using the quantum-mechanical CNDO/S3 model. An analysis of the geometric changes at the substitution site and its effect on the electronic structure allowed for the prediction of changes in the ICT bands of the optical
absorption and emission spectra. In particular, the red-shift of the low energy ICT absorption band can be predicted by analyzing the one-electron orbitals involved in this transition.

A second organic polymer which has found widespread use in microelectronics and medical technologies is polyethylene terephthalate (PET). The photo-physical properties of PET, for the most part, can be understood by considering PET as a perturbed benzene system. There are, however, certain elements of the emission spectrum which arise from intermolecular (chain-chain) interactions in the amorphous regions of the polymer film. In our current work, we have used empirical molecular dynamics simulations to investigate whether single strand of PET can fold in such a way as to allow different ends of the same strand to interact. The conformational flexibility provided by the saturated ethylenic linkage certainly makes this possible. Simulations on chains of 8, 16, and 24 unit cells in length were performed and the trajectories analyzed to determine if unit cells were able to approach and strongly interact. The results of the simulations indicated that although the single PET strand did fold into a helical conformation, unit cells never came sufficiently close to self-interact, indicating that the anomalous emission features must be associated with regions of polymer forced into energetically unfavorable local conformations as a result of the thin-film synthesis process.

Bulk and Surface Defects in Minerals: A New Electronic Structure Method

Defects play an important role in the bulk and surface chemistry of minerals. In fact, it has been argued that all of the interesting bulk and surface chemistry in these natural systems occurs at defect sites. The structure, atomic and electronic, of these active sites, however, is poorly understood, both experimentally and computationally. We have recently developed a real-space, first principles, electronic structure method, using the Harris-Foulkes energy functional and the recursion method, to compute the atomic and electronic structure of defects in mineral oxides which overcomes the problems described above. Because the recursion method is used to solve the Schrödinger equation in real-space for local properties, the method is computationally efficient—we have performed computations on clusters of 27,000 atoms—and the need for supercell networks of periodically repeated defects is eliminated, allowing the examination of isolated and charged defects. This method has been tested and validated by computing the electronic structure and stability of the perfect (001), (111)-Mg, and (-1-1-1)-O surfaces of MgO and using the local-density of states at the surface to understand the relative stabilities and differing electronic structures of the surfaces in terms of the different surface chemical bonding. The results are in excellent agreement with other first-principles methods and with experiment.

We have recently applied this method to the computation of the electronic structure and energetics of isolated bulk and surface oxygen vacancy defects (F centers) in MgO. Based upon atomic relaxation principles first elucidated in the study of semiconductor surface reconstructions, the atomic relaxation around these defects is expected to be negligible. The computed formation energies of isolated surface and bulk oxygen vacancy defects are 2.04 eV and 1.89 eV, respectively. The computed formation energies are in excellent agreement with the available experimental data which estimates a formation energy of 1.53 eV for the oxygen vacancy defect in the bulk material. Previous first-principles computations, using a supercell of 15 atoms (MgO$_2$), arrived at a value of 0.4 eV (Wang and Holzwarth 1990). Clearly, the interaction of the defects in this computation is too large to ignore. The computed and experimental formation energies of these defects are in strong disagreement, however, with the pair potential model of an ionic material which predicts a formation energy of 10.35 eV for a bulk oxygen vacancy. This disagreement can be explained in terms of the relaxation of the electronic wavefunction at the defect site which stabilizes the defect.

Reference


Publications


Mineral Physics and Chemistry Relationships

A. C. Hess (Chemical Structure and Dynamics)

The objective of this research was to gain a fundamental understanding of the physics and chemistry of clay minerals, such as kaolinites, smectites, etc., using state-of-the-art electronic structure and molecular dynamics techniques. This project focused both on the application of existing methodologies to specific oxide materials and the development of the next generation of theoretical methods. The proof-of-principles work necessary to gauge the behavior of the new theoretical methods was carried out on simple well-characterized systems and a realistic effort was made to apply the methods toward mineralogical systems important in the field.

Research during the past year has been directed towards modifying and improving the *ab initio* Periodic Hartree-Fock program CRYSTAL such that it can better solve problems of interest to DOE, and demonstrating the capabilities of the method by applying it to several complex geochemical systems. As stated in objective section above, LDRD-supported work focused on applying this method specifically to naturally occurring oxide minerals. Throughout these studies a large list of observable quantities have been computed and compared to available empirical data. These comparisons have allowed us to evaluate the overall performance and stability of the method with respect to a number of potentially problematic areas including, basis sets and truncation and tolerance schemes for evaluating various infinite series involved in the formal theory. In general, the method has far exceeded our initial expectations and has proven to provide an accurate and reliable means to investigate many systems of geochemical importance. Specific systems studied this year include the surface properties of several clay minerals (kaolinite, pyrophyllite, and talc), the adsorption properties of Cl2 on MgO surfaces, elastic and phase stability of zinc oxides, and various properties of the oxy-hydroxide boehmite.

Publications


D. M. Sherman and M. Causa, "Proton Hopping in Boehmite (g-AI0OH)" (in preparation).
Molecular Dynamics at Solid Surface Interfaces

J. P. Cowin and B. D. Kay (Chemical Structure and Dynamics)

This project was directed at creating methods to trace the molecular-scale steps required for surface transformations. These reactions include the poorly understood water/solid interface with its ionic, charge-transfer, and solvation processes. Mineral interfaces are especially important and among the most technically difficult to study. Enabling approaches to mineral interface studies in ultrahigh vacuum were pioneered, especially relating to the role of surface structure in breaking the chlorine-carbon bond in Hanford site species like chlorinated hydrocarbons.

Reactions at the water/solid interface are crucial to understanding both soil and atmospheric environmental reactions. Our efforts in FY 1992 were aimed at two areas: interactions of ions at these interfaces, and charge-transfer processes. In both studies, the water-solid interface is modeled using water multilayers adsorbed below 150K and down to 50K. At these temperatures, the vapor pressure of water is low enough to allow us to coat a normal sample (a 1-cm diameter disk) with arbitrary thicknesses of water. Other species are codeposited into the water film to recreate solid–aqueous interfaces. Using this technique, solvation and hydration processes, the electrochemical double layer, and ion-water-surface interactions can all be explored.

Several studies this last year examined water and other layers on a Cu(110) surface. In one study, we studied the co-adsorption properties of a hydrophobic chlorinated hydrocarbon molecule, CH₃Cl, and water. The thermal desorption characteristics of CH₃Cl after different initial coverages indicate strong self-repulsion in the first monolayer. If this experiment is repeated after first coating the surface with one monolayer of water, the binding energy of the CH₃Cl to the surface is greatly reduced for the first monolayer, and the self-repulsion disappears. These and other studies show how water and chlorinated hydrocarbons compete for binding on the surface.

To study the structural aspects of these multilayers, we constructed an ESDIAD (electron stimulated desorption/ion angular distribution) display, which also allows very sensitive low-energy electron diffraction. Our preliminary studies yielded patterns for water adsorption that are indicative of the orientation of the O–H bonds at the surface. Work is beginning on thin-film deposition of oxides on a refractory single crystal substrate, to provide convenient models of mineral-type surfaces.

Our studies of ions at surfaces involve a collaboration between PNL and the University of Colorado. An ion source being built there will be delivered to PNL for joint use. This source will be capable of producing intense beams of positive or negative mass-selected molecular ions for deposition at very low energies.

Publications


M. R. Schneider, C. P. Dehnhostel, T. L. Gilton, M. Kwini, and J. P. Cowin, "Photoelectron Induced Surface Chemistry: Methyl Chloride on GaAs(100)," *J. Appl. Phys.* (submitted).
Molecular Mechanisms of Carcinogenesis

J. D. Zimbrick (Biology and Chemistry)

The objectives of this project are to research the distribution and frequency of ras oncogene mutations in radon- and chemical-induced lung tumors in rodents, the development of DNA double-strand break and single-strand break, single-cell gel assays to measure the distribution of damage in cell populations after exposure to radon, and the evaluation of the effects of in utero (irradiation on the expression of fibronectin in the brain of mice.)

In FY 1992, ras gene sequences were amplified from the DNA of 13 radon-induced rat lung tumors and 3 plutonium-induced rat lung tumors. Sub-clones of these ras genes have been sequenced, and in three of the radon-induced tumors and one of the plutonium-induced tumors we have detected a transforming point mutation at codon 12. Preliminary evidence indicates that these mutations may be specific to the tumor types; all of the mutations have been detected in epidermoid carcinomas. No ras mutations have been detected in adenocarcinomas or in normal tissues.

We have used the alkaline single-cell gel (SCG) technique to provide a biological estimate of the percentage of cell nuclei "hit" by alpha particles during in vitro radon exposure. The profile of DNA migration in radon-exposed cells (39cGy) was bi-phasic, with one distribution corresponding to the control (non-irradiated) response and the other profile showing increased DNA damage. We interpret the second profile as representing cell nuclei that had received an alpha "hit." The percentages of cell nuclei in the "hit" category (approximately 51 and 45% of CHO cells and AL cells), as judged by the SCG technique, were 81 and 62% of the calculated values. We conclude that the SCG technique is useful for the evaluation of "hit" probability calculations relating to complex high-LET (linear energy transfer) radiation sources.

We have isolated insoluble matrix fraction and measured the amount of fibronectin (FN) in the insoluble matrix fraction by gel electrophoresis and Western blotting analysis. Total amounts of FN in the insoluble matrix fraction of mice brains at 17 days gestation were 1.66 ± 0.8 μg and 0.58 ± 0.22 μg for the normal and irradiated groups, respectively. They were significantly different between normal and irradiated groups (p<0.02). We have established Northern blot analysis to compare fibronectin mRNA between control and irradiated brains. Relative fibronectin mRNA expression was significantly reduced in irradiated brains after exposure to 0.5 Gy. We have also compared FN isoforms in control and irradiated brain at 17 days of gestation by two-dimensional electrophoresis. We have found that isoelectric point (pI) for the isoforms of FN in normal brain was in the range of 6.5 and was in the range of 5.5 for irradiated brain. The shift of pI in the irradiated brain indicates that prenatal irradiation modulates protein structure. We have concluded that prenatal irradiation reduces FN gene expression and protein levels.

Publications


Presentations


Molecular-Scale Investigations of Alkali Halides

R. L. Erikson (Geosciences)

This project focused on investigating relationships between molecular-scale interactions and the macroscopic properties of selected alkali crystals and melts. The work involved an examination of how well periodic quantum methods and statistical mechanics methods perform together in calculating thermodynamic and structural properties involving solid-state phase transitions, melting behavior, and phase equilibria in binary alkali halide systems.

Our initial investigation in FY 1992 focused on ab initio calculations of the solid-state B1/B2 phase transition in NaF. Basis set development methods for molecular cluster calculations were used to develop basis sets for periodic ab initio calculations of the energy-dependent properties of ionic crystals. Two extended Gaussian basis sets for closed-shell sodium and fluorine ions were developed to compare with two minimal basis sets in calculating the crystal structures, enthalpies of formation, and high-pressure compression behavior of the B1 and B2 phases of NaF. Accurate calculation of the energy-dependent properties to within experimental error required the use of the larger, extended basis sets. Enthalpies of formation for NaF-B1 at 0K and 1 bar were calculated to be between -921 and -929 kJ/mol, which agrees well with an experimental value (-927±10 kJ/mol) estimated from calorimetric data. For the B1 phase, the zero-pressure bulk modulus was calculated to be between 0.485 and 0.499 Mbar, as compared to the measured value of 0.464±0.062 Mbar. The calculated molar volume at zero pressure agrees to within 0.1% of the experimental value. For the B2 phase, the zero-pressure bulk modulus was nearly the same as that for the B1 phase, ranging from 0.494 to 0.517 Mbar. However, this calculated bulk modulus for the B2 phase was considerably smaller than the experimental value of 1.03±0.19 Mbar estimated from high-pressure compression measurements. Our calculations also suggest the V_{02}/V_{01} of the B2 phase is nearer to 0.871-0.895 than to the experimental estimate of 0.811. The compression curves for both phases agreed, for the most part, with the experimental data to within the experimental error. The calculated pressure for the NaF B1/B2 transition is between 0.26 and 0.29 Mbar, slightly higher than the averaged experimental value (0.23±0.03 Mbar) within a pressure range where both phases metastably coexist along the compression curve. The calculated volume change accompanying the phase transition (-10.1%) is in good agreement with experimental data (-10.4%). The apparent discrepancies between the zero-pressure bulk modulus and the compression curves of the B2 phase are shown to be related to the range of molar volumes used in deriving the zero-pressure properties from an equation of state.

Publication and Presentation


Multicenter Hazardous and Radioactive Waste Treatment

W. A. Ross (Waste Treatment Technology)

The objective of this project was to provide DOE with improved and cost-effective technologies to aid in the cleanup effort at the DOE sites (with special emphasis on the Hanford site). During FY 1992, activities within the project emphasized waste characterization and biosensor development, biological destruction of toxic wastes, waste separations, chemical destruction, electrical destruction, and systems engineering.

Integrated Characterization and Visualization System

This activity focused on providing a hardware/software environment for the storage, processing, analysis, and display of geophysical data collected for the characterization of hazardous or radioactive waste burial sites. This integrated environment was to be an interactive computer graphics based tool that will give geophysicists and others access to a powerful set of state-of-the-art capabilities for efficient data manipulation, modeling, and other necessary data processing procedures. Following are five recent accomplishments. 1) The project has successfully obtained three sets of geophysical data. This data included Ground Penetration Radar, Electro Magnetic Induction, and Magnetometry. 2) A basic visualization prototype has been developed utilizing the initial geophysical data sets. The current prototype provides basic viewing of the specific data, rudimentary viewing of combined data sets, three-dimensional manipulation, some features for extraction of the data, and hard-copy output. 3) The initial data sets have provided a basic understanding of geophysical structure. A preliminary structure design has been developed. 4) Information about site characterization for remedial action processes has been obtained and areas where the proposed system would help have been identified. 5) Possible links to the Remedial Action Assessment System (RAAS) have been identified.

Biosensors for Real-Time Monitoring of In Situ Bioremediation

A strain of bacteria which bioluminesce when metabolizing a hazardous compound, in this case naphthalene, was obtained. Efforts to insert the luxposon (the gene responsible for bioluminescence) into strains of bacteria with compounds such as trichloroethylene (TCE) were undertaken, but have not yielded positive results. Using colonies of the naphthalene degraders, the interrelationships between light output, viable cell numbers, and the naphthalene concentrations were measured. These experiments were performed using existing in-house light detection systems including an intensified video-based quantitative luminescence imaging system and a non-imaging photomultiplier-based system. The light levels encountered disclosed that optical detection of in situ bioluminescence will be very difficult due to the attenuation encountered in soils. Optical monitoring therefore does not look attractive based on the current state of light detection technology. Non-optical methods for in situ monitoring of bioremediation were then considered. However, sensors for the various indicators of bioremediation such as O₂, CO₂, pH, etc., were found to be well developed and commercially available, and no novel approaches were identified.

Vadose Zone Bioremediation

The objective of these experiments was to determine whether gaseous substrates and electron acceptors can be used to induce microbial activity in vadose zone soil. Experiments were performed to examine the feasibility of using gaseous substrates and electron acceptors to simulate microbial activity in the vadose zone by demonstrating substrate utilization with saturated vadose zone soil inoculum. The primary conclusions from this study are that nitrous oxide can be used as an electron acceptor by bacteria indigenous
to the vadose zone soil, however, it is not an assimilable source of nitrogen. Also trimethylamine can be utilized as a substrate under aerobic conditions, but utilization under denitrification conditions is either extremely slow or does not occur. Additionally propane, butane, and ethane cannot be utilized as substrates under denitrification conditions by bacteria indigenous to the vadose zone soil. While a suitable gaseous electron donor was not identified in this study, significant microbial growth was demonstrated using an aqueous electron donor and a gaseous electron acceptor (nitrous oxide).

Development of a Plant Rhizosphere-Based Containment and Biorestoration Technology

The objective of this activity was to identify opportunities and limitations to the use of plants for containment, bioremediation, and biorestoration at Hanford. Initial evaluation of the effectiveness of rhizosphere-mediated bioremediation was demonstrated. Spring wheat plants were used with native and genetically manipulated rhizosphere organisms that were shown to degrade the herbicide 2,4-dichlorophenoxy acetic acid (2,4,D). This same approach may be possible with TCE and other hazardous organic materials.

Tritium Removal from Waste Waters

The objective of this work was the development and evaluation of polymer membranes for use in the separation of tritium (THO) from ground waters (H2O) by prevaporation. The membranes used in the process were the key to its success. Polyphosphazines (PPO), a new species of polymer, were developed for use as a hybrid membrane that combines the robustness of a ceramic and the tailoring capability of an organic polymer. During the year, coating blocks and doctor blades were obtained from Eastman Kodak Company. A test cell was designed and fabricated and nine aryloxy polyphosphazene polymers were synthesized. A source of HTO containing ground water was also identified and samples will be obtained for testing during FY 1993.

Closed Chamber Electrolyte System for Nuclear Graphite Decontamination

The objective of this project was to demonstrate the feasibility of operating a closed cell system for the separation of graphite from radioactive materials. The concept involved the use of molten carbonate fuel cells and other components to incinerate contaminated graphite and with subsequent development, incinerate radioactive and hazardous organic materials in a closed system which uses the fuel cell to remove the carbon dioxide from the chamber. An extensive domestic search was conducted which identified sources of the carbonate fuel cells and technical expertise. The consultants confirmed that the cell would perform the desired filtering function and provided guidance as to some of the appropriate cell operating parameters. A test system design was developed and analyzed by a model. The model projects that a suitable system could process the 1600 metric tons of graphite for one Hanford reactor in one year. Laboratory demonstrations are needed for follow-on work.

High Overpotential Electrodes for Organic Destruction in Aqueous Solutions

The objective of this work was to develop new electrode surfaces that could be used in an electrochemical oxidation process for the destruction of organics. These new electrode surfaces would allow the electrochemical technologies to be used for organic destruction in Hanford tanks and in the future for waste water treatment in the private sector. Three new electrodes were developed and tested. Two of the electrodes show potential in the area of organic destruction. These new PNL-developed electrodes will allow the electrochemical oxidation technology to be competitive with alternative methods for waste water treatment and Hanford tank waste organic destruction.

Identification of Free Radicals for Low Temperature Plasma Discharges and Their Reactions

Experiments performed by this activity have shown that corona discharges above the surface of water effectively destroyed organic compounds dissolved in water. This was shown dramatically by the destruction of dye solutions which were bleached of color by the plasma discharges. Experiments were designed to quantify the yields and identify the oxidizing species produced by corona discharge. The results indicated that 50 to 150 ions were oxidized per electron discharged. The results depend on the gases present during the discharges. It was determined that ozone, hydrogen peroxide, and other species were produced. The information shows why few organic structures could resist the corona products and why the method works well for destruction of organic materials.
Micro-System Applications

Several concepts were considered for the application of micro-systems to waste processing.

Publications


Multivariate Adaptive Regression Spline (MARS) Approximation Methods

A. L. Liebetrau (Analytical Sciences)

The purpose of this project was to apply multivariate adaptive regression spline (MARS) methods to approximate the (output) response surface of complex computer codes with a large number of input variables or extremely long run times, or both. The approximations are used to perform simulations that would otherwise be prohibitive because of the long run times involved. Essential properties of the approximation were that it preserve the essential features of the underlying code, and that it runs much faster than its complex counterpart.

A series of runs were done for each code, and response surfaces were approximated using MARS. For comparative purposes, approximations were also done using classification and regression tree (CART) methods (CART and MARS methods are both extensions of classical linear regression, but the two approaches use different approximating algorithms). All methods produced essentially the same results for the EPIC code. However, the question of how to best deal with stochastic variability in the underlying code remains open. The CART approach worked better than the MARS approach for dealing with the zeros observed in the AREST code output.

Installing the MARS code and learning how to run it and interpret its output were important outcomes of this research exercise. From the exercises with the EPIC and MARS codes, we gained vital experience for developing approximations to other complex codes. As more and increasingly complex models are combined to produce "system" models, the need for computationally tractable approximating models will increase.

Presentation

Progress on this work was described in a professional paper entitled, "Modeling the Uncertain Impacts of Climate Change." The paper was presented at the Fourth International Conference on Statistical Methods for the Environmental Sciences, held in Espoo, Finland, August 17-21, 1992. It is currently planned to submit the paper for publication in Environmetrics.
Naturally Occurring Metal Chelates: Structure/Stability Relationships

B. P. Hay (Geosciences)

This project was directed toward the development of new theoretical methods, strategies, and capabilities to elucidate the effect of chelate architecture on metal binding affinity. The scope of this work is to research the possibility of using molecular modeling techniques to gain an understanding of the role that steric factors play in the stability of metal complexes with naturally occurring organic chelating agents.

The focus of this project was the use of molecular modeling techniques to gain a molecular level understanding of the metal ion binding affinities of naturally occurring organic chelating agents. Exhaustive literature surveys were conducted in the areas of molecular modeling techniques for coordination compounds, identity and structure of naturally occurring organic compounds, and structure/activity relationships for chelating agents. Key concepts from these three research areas were identified.

Naturally occurring organic ligands were found to play an important role in soil/groundwater equilibria. These ligands influence the weathering of soils and the mobility of metal ions. Factors controlling the stability of complex formation remain poorly understood. Prior studies have suggested that changes in ligand conformation that occur on complexation are an important contribution in determining complex stability. We propose to apply molecular modeling techniques to quantitatively examine conformational effects in the complexation of metal ions by organic acids and alcohols, functionality that is representative of the types of binding sites in humic and fulvic acids.

The computational model will be constructed by extending a molecular mechanics code for organic compounds to include the additional interactions that are present in metal complexes. The nature of these metal-dependent interactions will be elucidated through the application of quantum mechanics to a range of metal complexes with archetypical alcohols and carboxylic acids. The accuracy of the model will be established by calculating properties of the ligands and their complexes such as equilibrium structure, conformational populations, vibrational spectra, and rotational barriers for comparison with reported values. Molecular simulations with the verified model will be used to quantify the effect of chelate structure on complex stability.

Publication

Probing of DNA in Environmental Microbial Populations

R. J. Douthart (Life Sciences Center)

A new concept direct blotting electrophoresis device is being used to characterize the genome of microorganisms of importance in environmental remediation. Using this device, single-stranded DNA from sequencing ladders or restriction enzyme DNA fragments are electrophoresed onto a suitable deposition membrane attached to a rotating drum. The drum is easily moved to downstream processing units where detection and DNA probing can be done automatically. The objective of what was planned to be the final year of support was to apply the device to probing small quantities of DNA rapidly. However, technical difficulties forced design changes.

A series of experiments with dyes and DNA fragments, including successful DNA sequencing have proven the viability of the technology. However, two major technical difficulties have forced abandonment of the more conventional vertical design and caused us to modify the apparatus to a less conventional horizontal design (i.e., the attitude at which the electrophoresis plates impinge on the drum). The difficulties encountered using the vertical design are the entrapment of bubbles and a substantial temperature difference (≥30°) at the interface between plate and the drum.

The new horizontal device tends to allow bubbles to escape and is much easier to thermostat at the junction. The modifications took considerable time and the new design, although built and assembled, has not as yet been thoroughly tested.

Horizontal Drum Device
Radiation Induced DNA-Protein Cross-Links\textsuperscript{(a)}

D. L. Springer and C. G. Edmonds (Biology and Chemistry and Chemical Sciences)

A fundamental understanding of the relationship of histone modification to chromatin structure and its alteration through cell cycle or after 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 non-random and predictable. Furthermore, this consistency will also pertain in the course of modifications arising from response to chemical or radiation insult. For the proposed experiments, we will evaluate the similarities and differences in profile that arise in the normal cycle in cultured human cells and the differences that arise in response to chemical insult using electrospray ionization mass spectrometry and tandem mass spectrometry. We hope to demonstrate the feasibility of our ultimate goal to elucidate the full details of these processes. We hypothesize that there may be sensitive and predictive modifications that may distinguish natural and chemical or radiation-induced alterations in chromatin structure.

Experiments were conducted where ESI-MS analysis of untreated chicken erythrocyte histone H2B (Mr 13,780) and this protein exposed to 5 Gy of ionizing radiation in the presence of 100-fold molar excess of thymine were compared. In the mass spectrum of the treated protein, we were able to observe peaks which were near the expected incremental value for thymine-H2B adduct (observed increment 126.1 Da, predicted increment 125.1 Da). We also observed an additional species with an incremental mass of 140.7 Da whose structure is presently unknown.

In early March 1992, we became aware that the proposal submitted simultaneously to the National Institutes of Health on the topic of radiation induced DNA-protein cross-linked species had been favorably reviewed, and recommended for support with a tentative starting date of May 1, 1992. Our LDRD project was consequently rescoped, as indicated above, for the remainder of the fiscal year.

Histones, which together with other specialized proteins 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 through 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 remain to be elucidated.

Experiments on histones derived from chick erythrocytes demonstrated the special capabilities of electrospray ionization mass spectrometry for the analysis of the post-translational modification of these proteins. In the case of the core histones, H2B, H4, H2A, and H3, measured masses of the constituents of more or less complicated mixtures after isolation and HPLC purification are incremented from the masses predicted from the gene sequences by values which were precisely accounted by combinations of post-translational methylation and acetylation.

These results were further verified by the examination of histones isolated for human K562 cells grown in normal cell culture and in the presence of butyrate, a deacetylase inhibitor which results in the hyper-acetylation of nuclear proteins. After HPLC isolation, SDS-PAGE separations of these histones demonstrated that the proteins were intact but revealed no detectable difference between histones from control and butyrate-treated cells. Electrospray ionization mass spectrometry of these materials demonstrates significant increases in heterogeneity of the proteins consistent

\textsuperscript{(a)} In FY 1993 the name of this project will change to "Structural Studies of Modified Histone Species."
with increased levels of acetylation. Further elegant confirmation of this was possible employing the acid-urea and triton-acid-urea PAGE method of Panyim and Chakley which permitted the separation by virtue of effect of acetylation of a lysine e-amino group reducing the electrophoretic mobility of the histone by decreasing the net positive charge on the protein. Thus, for example, for histone H4, a series of four proteins from butyrate-treated cells was observed migrating at successively slower rates than the H4 species present in the normal control culture. 

Electrospray ionization mass spectrometry of histone H4 demonstrated the presence of a series of four additional proteins successively incremented from the control H4 mass by 42 D. The experiments provide strong evidence of multiple acetylation of histone H4 from butyrate-treated K562 and demonstrate the utility of electrospray ionization mass spectrometry in the evaluation of the nature and extent of this and other post-translational modifications.

Publication


Presentations


Radiative Forcing by Anthropogenic Aerosols

C. M. Berkowitz (Atmospheric Sciences)

The objective of this project was to describe the spatial variability of short-wave scattering by anthropogenic aerosols in the lower troposphere. An assessment of the magnitude and variability of this term as a function of spatial position helped in evaluating the significance of this term relative to warming associated with long wave absorption by greenhouse gases. The domain of the study was the North American continent, the Northern Atlantic, and Western Europe, making the results comparable with global scaling arguments previously used to establish this numerical equivalence between warming by greenhouse gas absorbed long-wave radiation and cooling by aerosol scattered incoming short-wave radiation.

Several weeks were spent studying the scientific literature related to climate change and aerosols. This was followed by a one-week visit to work with scientists at Brookhaven National Laboratory on combining a radiation transfer algorithm with the PNL model being used to evaluate the distribution of aerosols over the Atlantic. The aerosols being studied were those that would be associated with SO$_2$ emissions from North America. Brookhaven provided emissions data, meteorology fields, and computer facilities while PNL provided the transport/chemistry model and aerosol routines.

Meteorological observations taken on a 6-hour basis over observing sites in North American and Europe were incorporated into the PNL model and a simple radiation transfer code was used to analyze the results for the effect on short-wave scattering. Preliminary results suggested that the climatic effects postulated in the literature were not realistic as a result of the very heterogeneous distribution of the resulting scattering. The non-uniform distribution of aerosols (and hence the scattering) was thought to be related to the non-uniform distribution of point sources of SO$_2$ and cloud cover.

Management commitments during 1992 precluded PNL's scientific staff from seeing this work through to completion. These commitments have since been met, and staff is available to continue work on this program during 1993.

Presentation

Radiometry for Pacific Northwest Laboratory’s Gulfstream G-1 Research Aircraft

W. J. Shaw (Atmospheric Sciences)

The goal of this project was to install a measurement capability for short- and long-wave broadband radiation on PNL’s G-1 research aircraft. During this project, mounts were constructed on the top and bottom of the aircraft to which the sensors were attached for running signal cabling to the G-1’s data acquisition system.

The construction of mounts on the top and bottom of the G-1 for short- and long-wave broadband radiation sensors was completed in FY 1991. The installation was tested by mounting borrowed radiometers (the airplane currently has none of its own) for the G-1’s Kuwait mission. These radiometers required recalibration prior to their return to their parent project. This was accomplished during FY 1992 and the project was completed.
Real-Time Studies of Chemical Reaction Dynamics in Molecular Cluster Ions

D. Ray (Chemical Structure and Dynamics)

Chemical reaction dynamics in molecular cluster ions were studied by ultrafast (subpicosecond) laser techniques. A new understanding of reactivity, energy transfer, and chemical dynamics in microparticles and at interfaces resulted from the development of intense new sources of mass-selected clusters.

Previously, we used laser spectroscopic methods to study clusters of solvent molecules around and on prototype solutes. These clusters can be synthesized in sizes spanning the range from isolated molecules to bulk-like microrystals or droplets, and their study provides an explicit connection between microscopic and macroscopic properties. Of particular interest is the effect of solvation on chemical reactivity, both in the bulk limit and in small-scale environments relevant to interstices or to liquid-solid interfaces. Solvents of great practical importance are those which hydrogen bond, especially water. In such solvents, reactions involving generation or migration of charged species are among the most significant and also the most difficult to understand. This project addresses these issues via the study of excited-state proton transfer reactions in hydrogen-bonded clusters (usually water). In these reactions the "solute" molecule is selected for its increased acidity in its first electronic excited state. This allows the reaction creating a solvated ion pair to be initiated with a laser pulse, which in turn permits one to study the course of the reaction with a variety of spectroscopic methods.

The experimental apparatus for the project was assembled in FY 1992. This includes the dedicated cluster source, mass spectrometer, and dispersed or total fluorescence detectors; shared equipment includes synchronized multiple nanosecond dye lasers, a picosecond dye laser, and a time-correlated single-photon-counting system. The associated data collection and processing software are also complete.

We initially studied 1-naphthol*(H2O)n clusters, with n up to about 60. The smallest of these clusters are unable to stabilize the proton transfer reaction products, but are nonetheless of interest because they have simple structures which provide insight into the nature of hydrogen bonds, and which are amenable to theoretical treatment. We studied the ground-state vibrations of these clusters via nanosecond ion-dip spectroscopy, with particular attention to the intermolecular modes. The lack of solvation-induced driving force for the reaction is evident in the remarkably low activity of these modes in the spectra, but enough is observable to make contact with recent high-level ab initio calculations on similar systems. Some vibrations of the naphthol moiety itself exhibit ion-dip depictions of greater than 50%, indicative of fast relaxation processes in the ground electronic state, possibly due to the presence of low-energy pseudo-bath mode of the solvent cluster.

The larger clusters are known from fluorescence spectra to undergo the proton transfer reaction. Initial experiments addressing the dynamics of the reaction have been performed. The clusters were excited with 10 to 15 psec laser pulses, and the time dependence of the appearance of the product ion-pair fluorescence was observed with time-correlated single-photon counting. Fluorescence upon excitation near the low-energy edge of the cluster absorptions exhibits a slow rise with a characteristic time of around 150 psec, believed to be a direct reflection of the time scale for water-"solvent" reorganization, and much slower than observed in room temperature bulk water (about 35 psec). This is an indication that the clusters are in a "slushy" state, not rigid as in a crystal, but not fully fluxional as in a liquid. This is a manifestation of the extremely small size of these systems, which results in a smearing of normally very sharp phase transitions over a substantial temperature range, and gives us access to molecular processes that are ordinarily too quick to readily observe.

In an attempt to change reactor conditions in a controlled way, the clusters were also excited at energies about 1100 cm⁻¹ above the lowest absorption edge. The expected result was that this excess energy would rapidly flow into the water cluster, "melting" it further, and thus increasing the reaction rate.

Integrated Environmental Research 1.1.74
increased rate is indeed observed, but only after a
remarkable induction period of about 100 psec, a very
long time by the standards of intramolecular energy
transfer. After about 250 to 300 psec, the fluorescence
in both experiments assumes the same behavior, indi-
cating that only the initial stages of the reaction differ
in nature, and probably showing that there are qualita-
tively different processes involved at different times in
the reaction. Current ideas about the induction period
focus on the possible presence of another electro-
tronically excited state surface in the energetic vicinity
of the reactive surface and transfer of population
between the two.

These results demonstrate that ultrafast laser
spectroscopic techniques can elucidate the effects of
solvation on the reactivity of clusters of water
molecules surrounding an organic species, a system of
importance in our understanding of the behavior of
pollutants at liquid-solid interfaces and in soil
interstices.
Redesign of Biodegradative Enzymes: Theory Development and Coupled Theory-Experiment Approach

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

The goal of this project is to develop new theoretical methods, strategies, coupled theory-experimental collaborations, and laboratory (PNL) capabilities to uncover enzyme/protein structure-function-dynamics relations in order to better execute enzyme redesign to achieve desirable new and improved catalytic functionality and alternative properties. The primary focus of this project was on biodegradation of key DOE-site contaminants and environmental restoration of affected DOE sites. Specific research efforts included: testing of different mean-field statistical potentials, molecular target functions and virtual-atom representations; use of high-level wave functions to determine atomic multipoles for individual amino acid residues; development of the QMEF-MD code and semi-empirical Hamiltonians applicable to macro-molecular systems; development of the new computer programs to improve the analysis of simulated data for biomacromolecules; performance of long molecular dynamics simulations with different efficient phenomenological-molecular models on proteins; and continued study of the dynamic motions of relevant enzyme-ligand complexes.

The active site of cytochrome P450cam is deeply buried and no direct experimental evidence is available regarding substrate/product motion from the exterior to the active site. The access channel(s) of P450cam is probably very transient and is poorly understood. Of the possible conformational mechanisms that could be dynamically responsible for substrate movement through the access channel, local "hinge-bending" is quite possible. Due to the large size of P450cam and lack of any direct experimental data on such motions, we first focused attention in FY 1992 on validating simulation methods for discovering such transient motions on one of the best studied smaller enzymes known to exhibit hinge-bending, T4 lysozyme. We developed and applied a dynamical cross-correlation method on T4 lysozyme to gain a better understanding of possible hinge-bending motions. We now plan to use these methods on the biodegradative enzymes, cytochrome P450cam and alkane dehalogenase (both have buried active sites).

Cytochrome P450cam hydroxylates camphor forming 5-hydroxycamphor with essentially 100% regio-specificity, while norcamphor is hydroxylated forming three products (45% 5-, 47% 6-, and 8% 3-hydroxynorcamphor). Our previous simulations of norcamphor-bound P450cam predicted predominately (from 68% to 88%) 5-hydroxynorcamphor. One possible explanation for this discrepancy is that the simulations were performed using D-norcarnphor, while the experiments were conducted with racemic norcamphor. The suggestion that norcamphor is the D-isomer, was based on the similarity with the native substrate D-camphor. Indeed the reported crystallographic structure for norcamphor-bound P450cam models norcamphor as the D-isomer. Unfortunately, the two stereomers have never been separated. Three simulations each of the L- and D-isomers of norcamphor bound to cytochrome P450cam were compared to account for the effects due to substrate orientation and the assignment of random velocities. Our recent results show that the L-isomer of norcamphor is predicted to give rise to predominately 6-hydroxynorcamphor, while the D-isomer gives rise to mainly 5-hydroxynorcamphor. From this data, we infer that racemic norcamphor will give rise to non-racemic 5- and 6-hydroxynorcamphors after oxidation by cytochrome P450cam.

Before attempting to redesign the activity of P450cam for a substrate significantly different from camphor, we have chosen to first modify the specificity of P450cam for the substrate analogue norcamphor. Achieving such an intermediate goal will give us considerable confidence and guidance toward modifying the specificity of P450cam to initiate the degradation pathway for targeted pollutants. To date, we have made two predictions that were confirmed experimentally.

M. B. Bass, D. Filipovic, S. G. Sligar, and R. L. Ornstein, "Increasing the Coupling between Norcamphor Oxidation and NADH Reduction in the P450cam Reaction by Molecular Dynamics Simulation and Site-Directed Mutagenesis," *Protein Engineering* (accepted with revision).


Presentations


Scale Averaging of Effective Parameters: Synthetic Multiscale Simulation System Design

T. R. Ginn (Geosciences)

This project is directed toward gaining a better understanding of the scale dependence of effective parameters and of consistent ways to define and derive scale-conscious robust representative models, or "effective systems." The project focused on preliminary concept elucidation and demonstration wherein available theoretical and experimental tools are examined for incorporation into an investigative experimental system.

Support under this project during FY 1991 led to the completion and refinement of a new analytical tool. This tool is a new mathematical method for finding the parameters of models of groundwater flow which take the form of systems of linear differential equations. This new methodology is valuable because all conventional numerical approaches to the modeling of groundwater flow and contaminant transport (e.g., finite differences or finite elements) result in systems of linear differential equations. The refinement process took the method to the stage where it could be used as a tool for numerical laboratory experiments with the modeling of synthetic data. The work in FY 1992 centered on the design and implementation of these experiments.

During FY 1992, the prototype investigative experimental system was designed, constructed, and exercised. The components of the system are summarized as follows. Computer coding was developed to generate synthetic two-dimensional depictions of fractally heterogeneous media. The generation technique is based in percolation theory and the media is represented with "percolation clusters" on many scales, with fine or fine-scale resolution. This medium is then used in a program which simulates transient flow through the synthetic system. The transient pressure heads from this simulation are then "measured" from only a few limited wells (points in the percolation domain), and finally the inverse/calibration method developed in FY 1991 is applied to these pseudo-measured heads to determine approximate depictions of the percolation cluster-based geological field, with only coarse or large-scale resolution. Exercises with this system are ongoing and have already been productive in their contribution to the second branch of progress.

The second area of progress involves a return to theoretical foundations of flow and transport theory, with direction partly from results of the aforementioned experiments. One qualitative result of preliminary experiments with the prototype system is that we found effective parameters on the large-scale resolution of the flow domain to exist only for "nonlocal" manifestations of the original linear system of differential equations. This indicator prompted collaborative effort with Professor John Cushman of Purdue University who had been working on nonlocal hydrodynamic processes. This collaborative effort resulted in a new rigorous and fundamental theory for nonlocal dispersion in heterogeneous porous media, and a manuscript on the result has been submitted for publication. This work is based in statistical mechanics and applied mathematics.

Publication

Site Specific DNA Damage by Radiation and Chemicals

D. L. Springer (Biology and Chemistry)

The objective of this project was to determine whether DNA which is modified with a chemical carcinogen has altered susceptibility to radiation damage, and sequence-related factors are involved in the production of base damage by ionizing radiation. These studies are driven by the fact that humans are not exposed to single carcinogenic agents but rather a variety of agents including chemicals and radiation, and therefore basic information on the potential interactions between these agents is needed. This hypothesis is supported by studies suggesting that chemical carcinogens and x-rays may act synergistically to cause malignant transformation. A number of mechanisms may be involved in such interactions; however, this project was focused on the hypothesis that the presence of chemical lesions on DNA alters the susceptibility of DNA to damage by ionizing radiation.

Several lines of evidence support the hypothesis that chemical lesions on DNA may alter its susceptibility to radiation-induced base damage. For example, studies suggest that local conformational changes in the DNA helix alter the susceptibility of those regions to radiation-induced damage. The benzo[a]pyrene diol epoxide (BPDE) adduct is known to cause local alterations in DNA structure, and thus may render this local region more susceptible to further damage by radiation. In addition, studies indicate that charge transfer (electron migration) occurs in DNA after irradiation. Since the planar pyrene ring of the BPDE adduct contains π electrons that can interact with DNA bases, it is conceivable that this adduct may interfere with, or "direct" damage produced by radiation-induced charge migration. Thus, we hypothesize that the presence of BPDE adducts on DNA may alter the local susceptibility of the DNA to damage by subsequent exposure to ionizing radiation. If true, this hypothesis has significant implications to the mechanisms by which chemical carcinogens and ionizing radiation interact in the carcinogenic process.

Our approach involved the synthesis of model oligonucleotides containing single guanine and thymine residues (5'ACACACTGACAC). The single guanine residue was the target of modification by BPDE, while the thymine residue served as an "indicator" of radiation-induced damage (i.e., thymine glycol formation). Initial studies were conducted with the thymine residue directly flanking the modified guanine. Methods used for the modification, purification, and characterization of BPDE modified oligonucleotides were developed in our laboratory during the last year. For this, the oligonucleotides were reacted with BPDE and the modified DNA separated from nonmodified DNA by reversed-phase HPLC which produced 10 to 15% yield of modified DNA. Since reaction of DNA with (+)anti-BPDE results in four stereochemically distinct adducts, we have enhanced the HPLC purification scheme such that we can now separate individual stereoisomers of the BPDE adduct. Characterization of the adducted DNA were by UV spectroscopy which demonstrated the presence of the adduct. Results from electrospray ionization mass spectrometry of the modified oligonucleotide appear promising and will provide conclusive information on the extent of addition.

Initial studies of radiation-induced damage in nonadducted oligonucleotides (5'ACACACTGACAC) designed to determine a minimum amount of DNA needed to measure base damage products after irradiation at 100 Gy have also been completed. The modified oligonucleotides were analyzed by gas chromatography-mass spectrometry methods. Using as little as 10 μg DNA, we were able to measure base damage products, including 8-hydroxyguanine. However, the yield of thymine glycol found in these samples was surprisingly low, since previous studies (Fucirelli et al. 1990) suggest that under these conditions, the yield of thymine glycol and 8-hydroxyguanine from irradiated denatured calf thymus DNA were approximately equal. This led us to hypothesize that the yield of base damage products is influenced by surrounding DNA sequence. Further studies using oligonucleotides with a single thymine flanked by either adenine, guanine, or cytosine on the 3' side showed that after irradiation, the presence of a 3' flanking guanine led to significantly less thymine glycol formation than the presence of 3' flanking
adenine or cytosine. Additional studies with the thymine shifted in the sequence away from the modified guanine are under way to determine spatial limits and possible directionality of the interactions. If further experiments substantiate these results, this will be the first report, to our knowledge, of sequence-related effects on radiation-induced base damage. Such studies along with experiments to determine the influence of chemical adducts on radiation induced base damage are planned for FY 1993.

Reference


Presentations

Solid Waste

G. M. Holter (Waste Systems)

The goal of this project was to identify and propose approaches to address current and future impacts at the regional, national, and international level that can result from solid waste management practices. Although solid waste management decisions are made predominantly at the local, county, and state levels, the cumulative result of such local decisions can have much broader impacts. Examples of relevant categories of impacts are resource depletion, environmental degradation, and reduced national competitiveness (through economic inefficiencies). There is currently a lack of a systematic approach to solid waste management at all levels. This project was intended to address this by providing the necessary basis and the analytical tools to perform systematic evaluations of the performance of the solid waste management system under various scenarios. Included among these tools is a comprehensive model of materials flows within the national solid waste management system.

During FY 1992, management practices for both collectively managed solid wastes (e.g., municipal solid wastes) and independently managed solid wastes (e.g., industrial solid wastes) were reviewed to provide a basis for determining an appropriate, integrated approach for analysis of current and future impacts resulting from them. It was determined that a basic necessity was to be able to address the issue of solid wastes within the broader context of materials production and use within our society, with consideration of the patterns of production and consumption that give rise to the wastes. Thus, a capability to predictively model material and waste flows at the macroscopic level needs to be developed, and this capability can later be coupled with other types of information to calculate the full range of impacts from solid waste management activities. This, in turn, will establish a basis for the analysis of alternative solid waste management scenarios, to assist policy and decision makers in establishing appropriate solid waste management strategies and approaches. It will also provide an enhanced basis for identifying important and impactful solid waste technology development opportunities.

The basic direction and approach for Macro Material Flow Modeling was identified during FY 1992. This direction and approach were developed into a modeling concept and documented in a comment draft report at the end of the fiscal year (to be completed and published during early FY 1993). In addition, a preliminary evaluation was conducted of available data on solid waste quantities and compositions to support the modeling activities; this preliminary evaluation was also documented in the same report. This report provides the basis for activities to be conducted in FY 1993 and beyond. The major focus of Macro Material Flow Modeling efforts is initially placed on municipal solid waste (MSW) and other collectively managed solid wastes (CMSW). However, the ultimate goal is to expand these efforts to include the full breadth of solid waste, including industrial solid wastes and other independently managed solid wastes (IMSW).

Several technical papers addressing the technical approach and the modeling concept were also developed during FY 1992 and submitted and accepted for presentation at national and international conferences on solid waste management and secondary materials.

In addition, a preliminary evaluation was conducted of available data on solid wastes to support the modeling activities; this preliminary evaluation was also documented in the same report. Several technical papers addressing the technical approach and the modeling concept were also submitted and accepted for presentation at national and international conferences on solid waste management and secondary materials.

Presentations


Spectroscopy Techniques for Analysis of DNA Damage

A. F. Fuciarelli (Biology and Chemistry)

This project is directed toward developing and applying gas and liquid chromatography-mass spectrometry methodologies to the analysis of molecular damage to DNA following exposure to free radical-generating agents, such as ionizing radiation and selected chemicals. Development of analytical techniques capable of characterization and quantitation of specific molecular products formed in DNA following exposure to free radical-generating agents provide methodologies capable of addressing fundamental questions related to the molecular mechanisms by which ionizing radiation and oxidative agents interact with DNA. An understanding of the mechanisms of damage induction, particularly in the cellular environment, is essential to advancing the knowledge base for studies in repair, mutagenesis, transformation, and cell death.

Electron Migration in DNA

The possibility for radiation-induced damage to manifest itself distal to the initial point of energy deposition in DNA has been an intriguing question. Solid-state studies have indicated that the migration distance of electrons, possibly through the "tunnel" created by the overlapping pi electron clouds of the purine and pyrimidine bases stacked into the DNA double helix, is on the order of 10 to 100 bases. Therefore, two of our major goals for FY 1992 were to: 1) investigate, characterize, and quantitate DNA products induced by interaction with hydrated electrons generated from exposure of aqueous solutions of mononucleotides and 2) to evaluate 5-bromouracil-containing synthetic oligonucleotides as model systems to address the distance, directionality, and influence of base sequence with respect to electron migration in DNA irradiated in aqueous solutions.

In FY 1991, we developed methodology incorporating high-performance liquid chromatography to investigate the potential for electron transfer between purine and pyrimidine bases irradiated in aqueous solutions using radiation-induced uracil formation from 5-bromouracil as a probe of electron interactions. We confirmed that uracil formation measured under these conditions could be used as a quantitative indicator of electron transfer reactions. In FY 1992, we performed experiments in which we used a competition kinetic analysis to estimate the yield of uracil following irradiation in aqueous solutions containing DNA bases (or deoxynucleosides) and bromouracil. Our data revealed that electron transfer occurred from the thymine or adenine radical anions to bromouracil, leading to an increase in uracil formation above that predicted from competition analysis, but not from guanine and cytosine for both DNA base and deoxynucleoside model systems.

Examination of electron migration in synthetic oligonucleotides required the development of gas chromatography-mass spectrometric methodology to assess yields of uracil in irradiated bromouracil-containing oligonucleotides and the application of DNA synthesis protocols for generation of oligonucleotides of defined base composition. Successful development of these methodologies permitted us to measure the yield of uracil as a function of radiation dose under conditions where the oligonucleotides were irradiated in their single- or double-stranded form following annealing with appropriate complementary sequences. In a set of oligonucleotides containing bromouracil at selected positions with G, A, T, or C spacers (i.e., [BrU(GGG)]3), significant differences in uracil yields were observed suggesting that electron migration occurred to different extents amongst oligonucleotides containing different base sequences. In single-stranded oligonucleotides, the yield of uracil in the irradiated model oligonucleotides decreased in the following order A>T=C=G. However, in double-stranded oligonucleotides, the yield of uracil decreases in the following order G>T=C=A.

Although electron affinity (T>C>A>G) may play a role in the transfer/migration processes, we are exploring several alternative explanations for these results.

Radiation-Induced Intramolecular Cross Linking Reactions in Nucleic Acids

Formation of (R) and (S) 8,5'-cyclonucleotides in nucleic acids are examples of intramolecular cross linking reactions induced by ionizing radiation.
Despite our predictions and measurements on the relative yields of these products, a report from another laboratory suggests that both epimers are formed in similar yields in double-stranded DNA. Molecular modeling studies that we have completed with Dr. M. Kennedy (University of Washington) during FY 1992 support our predictions that the S epimer should not be formed in double-stranded DNA because a major structural perturbation is necessary for appropriate positioning of the carbon moieties for cross linking to occur. We are attempting to resolve this apparent discrepancy by measuring the yield of (R) and (S) 8,5'-cyclopurines in DNA and oligo- nucleotides of defined base composition using both gas and liquid chromatography-mass spectrometric methodology. This work falls under our proposed objectives of using synthetic oligonucleotides to address the issues of damage induction and distribution as a function of primary sequence and measuring DNA damage at low radiation doses. Synthesis of these products is required to obtain authentic compounds for quantitative mass spectrometry and for use in preparation of oligonucleotides containing such products. We have initiated this synthesis in collaboration with Dr. J. A. Raleigh (University of North Carolina, Chapel Hill) in an effort to develop a routine synthetic strategy that will enable us to meet our research objectives detailed in proposals that we have submitted to DOE/OHER and NIH which feature these unique DNA modifications in structure-function studies incorporating computer modeling, spectroscopy and molecular biology studies.

Publication


Presentations


Structure/Function Studies of DNA Repair Processes

J. D. Zimbrick (Biology and Chemistry)

The objective of this project is to identify, define, and characterize components of the mammalian cell DNA repair systems involved in reversing radiation- and chemically-induced DNA damage. Particular emphasis was placed on studies to elucidate the perturbations in DNA structures containing these damages. Related studies centered on the physical chemistry of the recognition/binding processes by which repair enzymes form complexes with substrate lesions and remove or repair them. Initial studies focused on a particular lesion formed when a purine base is removed from its DNA site by the action of radiation or chemicals.

Studies to date have focused on the synthesis and purification of short segments of DNA (oligomers) with defined purine and pyrimidine base sequences. Lengths of 4 bases and 6 bases have been produced (tetramers and hexamers, respectively). These oligomers have been irradiated and purified such that only one specific lesion/oligomer exists in each batch of purified sample. This process is continuing in order to accumulate sufficient mass in each sample for two-dimensional NMR analysis of structural perturbations.

These damaged oligomers have also been subjected to the action of a common DNA enzyme (nuclease I) which cuts the molecules into their individual base components. It has been found that this enzyme is not able to act on some of the radiation-induced lesions in the oligomers. For example, the enzyme cannot cut off formamidopyrimidine lesions and is not efficient in cutting off thymidine glycol lesions, but is efficient at doing this for dihydrothymidine lesions.

Presentations


J. M. Falcone and H. C. Box (Roswell Park Cancer Institute, Buffalo), and John Zimbrick, Pacific Northwest Laboratory, "Studies of Enzyme-Substrate Interactions Involving Nuclease P1 and Short Sequence Oligomers of DNA."

A. F. Fuciarelli, E. C. Sisk, and J. D. Zimbrick, Pacific Northwest Laboratory, "Electron Transfer in γ-irradiated Solutions of DNA."

E. A. Schroder and H. C. Box (Roswell Park Cancer Institute, Buffalo, NY), and J. D. Zimbrick, Pacific Northwest Laboratory, "Short Sequence Oligomers of DNA for Genotoxicity Studies."
Synchrotron Research/Advanced Photon Source Beamline

B. R. Stults (Macromolecular Structure and Dynamics)

This project is intended to develop an advanced capability using synchrotron radiation at the National Synchrotron Light Source (NSLS) to perform structural measurements at environmentally important interfaces and complete preconceptual design for new beam lines at the Advanced Photon Source (APS) at Argonne. The project will provide proof of principle that a new beam line at the NSLS is capable of measuring elemental concentrations and distributions at environmental interfaces with unprecedented resolution.

In FY 1992 efforts were devoted to exploring several applications of synchrotron radiation for the study of environmentally important materials. Feasibility experiments were initiated to establish the suitability of experimental stations at NSLS for the study of species found in very dilute concentrations. In collaboration with Dr. J. Linehan, we have explored the use of the x-ray absorption fine structure (XAFS) technique to characterize the formation of nanoscale metal oxide clusters. XAFS measurements were performed on iron oxide clusters prepared with the MRM and Rapid Thermal Decomposition of Precursors in Aqueous Solutions (RTDS) methods and MRM particle formation in situ measurements were recorded. In addition, small angle x-ray scattering techniques were used to measure the size of the clusters. The large amount of data is presently being analyzed but preliminary analysis looks promising. In FY 1993 we plan to extend these studies to other clusters, such as Fe-S, Zr-O, and Ti-O.

In another study, we investigated the local environment of Pb in contaminated water. Because of the dilute concentration, fluorescence detection techniques were used. These experiments were not successful due primarily to NSLS beam line design. We have proposed changes to the design of X8C beam line and in FY 1993 plan to repeat the Pb experiments and use fluorescence measurements to study the locations and movements of contaminants in clays.

Because of the deep penetration of the x-ray, photon-in-photon-out techniques such as x-ray Raman spectroscopy are expected to play a big role in the characterization of the environmental materials. We have initiated studies of soft x-ray emission using synchrotron radiation excitation and discovered that this process can be best interpreted as an inelastic scattering process. This new understanding of x-ray absorption and emission processes in terms of resonant inelastic scattering has profound implications. This work is preliminary and we are looking to extend the work to the hard x-ray range and exploring its use in studying environmental materials.

With Professor E. Stern (University of Washington) and other collaborators, tests were initiated to examine the feasibility of using tapered glass capillaries for focusing x-rays. An alignment problem, mostly dealing with the handling of the capillaries under ultrahigh vacuum condition, has been encountered and we are currently designing a new alignment system. This will be a major focus of our work in FY 1993 because the capillary focusing technique is critical to our beam line designs for the APS.

We participated in the construction and maintenance of the soft x-ray undulator beamline X1B. Because of our efforts, X1B achieved the best resolution and intensity in the soft x-ray region currently available in the world. Since it covers the transition metal L-edges, soft x-ray is expected to be very useful in studying impurities in solids and solutions (e.g., proteins).
Technological Response

W. B. Ashton (Technology Management Planning)

This project is directed toward the performance of studies and computer model development to improve understanding of how long-term structural changes driven by technological progress can be expected to affect global environmental processes. The focus of the Technology Response work is on “integrating” aspects of the theme, not simply investigating particular technology "fixes" to limit adverse environmental impacts. Two research themes were pursued in this work: How Can We Forecast the Impact of Structural Changes on Natural Global Environmental Systems?, and, How Can Structural Changes Be Used to Implement Sustainable Development Practices in Concert with Global Environmental Systems? Specific research activities to address these themes included: 1) developing a systems dynamics model of technology in the global carbon cycle; 2) studying the potential for carbon sequestration in the industrial and utility sectors; 3) modeling the global food and biomass production system; and 4) exploring the environmental gains from improved community system design and operation.

Technical progress for each of the four main areas in the Technology Response research program are summarized below:

A Systems Dynamics Model of Technology Impacts in the Global Carbon Cycle

The objective of work on the global carbon cycle is to develop and test a dynamic systems model of the global carbon cycle for use in evaluating the potential global effects of technology response options to mitigate GHG emission increases. The goal is a model that will permit aggregate analysis of broad technology responses to GHG releases (e.g., scrubbing carbon from fossil-fired point sources) and to support carbon cycle modeling in the SGM. During FY 1992, an executable FORTRAN module of Version 0.0 of a 20-region Global Carbon Model was produced. This code represents a computer model that can stand alone or that can be adapted for incorporation into the SGM. It was built by modifying an existing modeling code and global terrestrial and ocean data bases (based on work by Jan Rotmans 1990; IMAGE: An Integrated Model to Assess the Greenhouse Effect. Kluwer Academic Publishers. Dordrecht, The Netherlands).

The Potential for Carbon Sequestration in the Industrial and Utility Sectors

Two efforts have been undertaken in this area because of its potential importance in technology responses and because little work has been done until recently. These efforts are summarized below:

- Sequestration in Chemical Products

During FY 1992, this work showed that carbon dioxide, which does not form a polymer by itself, can be used with other chemicals to make a lightweight, strong, and economic alternative to silica-based building structures. Polycarbonates which contain up to 90% by weight of carbon dioxide and which are strong enough to be used in building and manufacturing applications have been made by gas microbubble impregnation technology. Moreover, the organic co-monomers which are reacted with carbon dioxide to form the copolymers can themselves be made directly or indirectly from biomass rather than from fossil fuels if required.

- U.S. Sequestration Supply Curve

In the second project, work was initiated to develop a U.S. national "CO₂ supply curve" that identifies the amount of CO₂ that can be captured as a function of the cost per unit of CO₂ controlled. This information will be used along with similar information on other CO₂ control options (e.g., carbon taxes, conservation, etc.) to help evaluate the best mix of policy options. During FY 1992, cost estimates were developed for sequestration of carbon via scrubbing at over 300 hypothetical U.S. utility power plant sites (over 800 gasification combined cycle-GCC units). The principle findings are the cost results, which indicate that the cost of CO₂ recovery can be much lower than expected. Levelized costs in real 1990 dollars of $0.0631/kWh (for a base case GCC plant with no CO₂ recovery), $0.0863/kWh to $0.1265/kWh (for ocean
Modeling the Global Food and Biomass Production System

Some technology research has been devoted to an assessment of potential environmental implications of increased demand for biomass (for energy, feedstocks, and food), in light of the need for long-term sustainability of a global-scale biomass system. The work takes a systems perspective by including consideration of environmental impacts from biomass production, distribution, storage, conversion, use, and disposal. In the fall of 1990, a workshop was held in conjunction with the University of Kentucky to examine the research issues associated with large-scale biomass utilization. It was concluded that there was need for a new regional scale energy, economic, and environmental model of the entire agricultural enterprise linked to the remainder of the ecosystem to realistically address the issue. During FY 1992, a draft working paper was produced to develop the issues and identify research opportunities and The Integrated Earth Modeling Consortium (TIEM) consisting of six major agricultural universities and PNL was organized for developing an integrated earth system model to fill the need identified in this research.

Environmental Gains from Improved Community System Design and Operation

To begin research on the role of urban areas in global environmental changes, a technology analysis has been undertaken to assess the opportunities for improved community design practices to implement sustainable development principles, thereby cutting resource use and environmental impacts. The project also seeks to describe the potential global economic and environmental benefits and costs of these practices, and to identify research needs to further investigate methods communities can use to capture the potential gains. In FY 1992 a draft paper, based on technical literature and conversations with experts, was produced. The research describes several U.S. cities with attractive design and operating features characteristic of "integrated communities." Several technologies that are particularly advantageous in energy-efficient communities were identified and characterized. Barriers to emergence of integrated community systems were also discussed.

Publications


Terra Vision

P. Van Voris (Global Studies Program Office)

The objective of this project was to investigate the possibility of developing the first quantitative spatially distributed tool for the analysis of the ecological impacts at the landscape, regional, continental, and global environmental scales. The tool consisted of: computer software incorporating a resource dynamics forest growth model; a geographic information system; regional scaling techniques; and a multi-level graphics display capability which could be used as a comprehensive management and decision tool (Terra Vision: "Terrestrial Environmental Resource Risk Assessment - Computer Visioning System").

The development of the multi-level graphics display capability was completed during FY 1992. Other project tasks, including the development of the forest growth model, were completed in previous years. The entire project is now complete.

Publication

A manuscript has been accepted by Cornell University for publication.
Training Initiative for Managing Highly Hazardous Chemical Processes

T. W. Yarde (Nuclear Systems and Concepts)

The objective of this project was to develop a systematic model for managing highly hazardous chemical processes while ensuring the model is consistent with the requirements in the final 29 CFR 1910.119, "Process Safety Management of Highly Hazardous Chemicals." Another objective of the project is to validate the model through extensive professional peer review and a process demonstration project.

The Vital Integration of Safety Information with Operational Needs (VISION) model was completed, and initial meetings were conducted to initiate a demonstration project.

The VISION model is a systematic depiction of the process of establishing an Occupational Safety and Health system that is consistent with the most recent systems thinking and in compliance with the most recent U.S. DOE Order concerning Occupational Safety and Health Programs (DOE Order 5483.XX DRAFT).

VISION uses the U.S. Department of Labor Safety and Health Program Management Guidelines published in Federal Register Vol. 54 No. 16 by incorporating the Guidelines' four major elements: management leadership and employee involvement, work-site analysis, hazard prevention and control, and safety and health training. It also depicts basic organizational relationships, information needs, facility systems analysis of processes and operations, work-site hazard analysis, risk assessment determination, hazard abatement, and safety and health program requirements.

The basic VISION model can be adapted to focus on any particular process, operation, or facility and to establish a system that will meet the requirements for a comprehensive Occupational Safety and Health Program while integrating other mandatory requirements.

In March 1992, direct funding from the DOE Office of Environment, Safety, and Health (DOE-EH) was received for a project that was similar in nature to the LDRD project described here. As soon as we became aware of this direct funding authorization, the LDRD project was discontinued. Some of the concepts developed in the LDRD project were utilized by DOE in developing the Work Statement for the EH project. Thus, the LDRD project resulted in the development of useful initial concepts, that were further explored using direct DOE programmatic funds.
1.2 Process Science and Engineering
Advanced Catalysts and Catalytic Processes

J. L. Bates and L. R. Pederson (Materials Sciences)

The goal of this project was to advance catalytic research. The project initiated research into new, advanced, and emerging catalysis concepts that emphasize the combinations of catalysis with other separation and reaction methods, and into non-metallic, inorganic catalysts as alternatives to the noble and transition metal catalysts. This includes research in areas of catalyst synthesis and characterization and catalytic reactions and mechanisms.

In FY 1992, synthetic methods were devised to prepare novel solid superacids by modification of metal oxide surfaces. These materials are potentially useful in catalyzing alkylation, isomerization, and other reactions necessary to upgrade fossil fuels. Solid acid catalysts are an environmentally attractive alternative to sulfuric and hydrofluoric acid catalysts currently used by industry on a large scale. Research during the past year focused on tailoring the activity, selectivity, and stability of these catalysts, and was conducted in collaboration with Washington State University. Apparatus was assembled that allows the activities of catalysts to be assessed in a manner accepted by industry. Contacts were established with several petrochemical corporations to better define research needs.

Solid superacid preparation methods included hydrolysis of metal nitrate(s), pillaring of certain clays by combustion synthesis methods, followed by treatment with an inorganic acid and calcination. Combustion methods were developed previously at PNL, and offer the advantage of essentially one-step preparation of high surface area powders from the precursor. Several of the products exhibited superacid character, as determined by reaction with Hammett indicators, a series of organic bases. Surface areas, pore sizes, crystal structures, and surface compositions and chemistry were among other properties that were determined for these catalysts.

One mixed metal oxide catalyst composition that was prepared by this project showed exceptionally high selectivity for the isomerization of n-butane to iso-butane, a critically important reaction. That is, virtually no cracking or dehydrogenation reactions occurred simultaneously with isomerization. The catalyst was also highly active in isomerizing n-butane, even at room temperature. Further evaluations of this particular catalyst composition are under way to verify these quite promising results.
Advanced Coatings

G. L. McVay (Materials Sciences)

The current biomimetic, organic, and inorganic polymer coatings techniques are based upon understanding gained from research programs which currently are conducted in laboratory-scale (beaker-size) experiments. The goal of this project was to test coating capability on irregular-shaped parts and scale the process up to pilot-scale size (approx. 2 feet x 2 feet x 4 feet). Scale-up activities required fluid dynamics input, sensor and temperature control over large volumes, and maintenance of precise levels of supersaturation.

Irregular-Shaped Parts

We have successfully demonstrated the capability to coat irregular-shaped parts using the biomimetic film process. Complex-shaped polystyrene (PS) parts containing internal and external corners, holes, and pins were formed by injection molding. The surface of these PS parts was then sulfonated, and the parts placed in mineral deposition solutions. Uniform coatings of FeOOH and SnO₂ have been deposited to date. Optical and scanning electron microscope microscopy on fracture surfaces and polished sections was used to verify the uniformity of the ceramic thin film. This is a significant result because it verifies our hypothesis that the biomimetics process is well suited for coating irregular-shaped and/or microporous substrates.

Mechanical Testing of Thin Films

We have also developed testing capabilities to measure the mechanical properties of our thin films. Film adhesion measurements are currently being performed using adhesive tape tests and tensile pull-off tests. To date, none of the FeOOH or SnO₂ thin films on sulfonated PS have failed the adhesive tape test. Preliminary findings of the tensile pull-off tests are also very encouraging. There have been no incidents of film failure without subsequent removal of the substrate (PS) surface. This implies that failure occurs in the underlying substrate rather than at the thin film-substrate interface. Again, we emphasize that these findings are preliminary until a detailed analysis of the fracture surface (by scanning electron microscope) has been completed.

We have also obtained a commercially available instrument for measuring the abrasion resistance of thin films and have begun chemical testing of coatings on polymers using an ASTM D-1308 standard test method.

Abrasion-Resistant Coatings

We have successfully developed surface modification schemes and solution deposition parameters for the formation of alumina precursor films on polycarbonate. The deposited film is not well characterized but seems to contain amorphous and crystalline aluminum hydroxide. Attempts at low temperature conversion of precursor phases to alpha alumina using base hydrolysis and hydrothermal treatments have been unsuccessful. It is unlikely that alumina formation will occur without high temperature (900°C to 1000°C) calcination.

In a continuing effort to develop chemical- and/or abrasion-resistant coatings, we have deposited dense, crystalline tin oxide films on sulfonated PS thin oxide films on molten PS Thin oxide films have excellent chemical resistance and moderate hardness (Moh’s hardness of 7). Development of SnO₂ thin films as potential chemically resistant and abrasion-resistant coatings is continuing. We have also deposited amorphous silica coatings on the surface of sulfonated PS. Amorphous silica films are transparent and reasonably hard (Moh’s hardness of 7), and may provide a workable coating for optical applications.

Process Scale-up

To address the issue of process scale-up, two fundamental questions must be answered. First, the kinetics of film formation must be determined, and second, a feedback mechanism (solution pH, ion concentration, etc.) must be selected before continuous processing is possible. To measure film deposition rates, a quartz crystal microbalance has been developed to operate in a flow-through cell and allow direct measurements of
mass deposited with time. To determine possible process control parameters, a detailed investigation of tin hydrolysis and condensation reactions has begun. Thermodynamic calculations combined with Fourier transform infrared and nuclear magnetic resonance are currently under way to determine the solution speciation and possible chemical reactions in the tin/water system. This information is necessary to optimize film deposition and to establish a feedback mechanism to control a continuous reactor.
Electronic Synthesis: Polymer Multilayer Thin Film Deposition

J. D. Affinito (Materials Sciences)

The goal of this project is to reduce to a manufacturing process, the technique of polymer multilayer (PML) flash evaporation of acrylic polymer thin films for energy conservation; lithium polymer batteries; optical, electronic, and nonlinear optical applications; and to do this in a manner consistent with simultaneous deposition of other thin films, by standard techniques, in a single chamber, in-line system.

This project is a continuation from FY 1991. During FY 1991, a vacuum roll coater was to reduce the PML process to manufacturing practice for the production of optical multilayer thin films. The equipment provided for computer-controlled substrate handling and process automation. The software control system was set up and some monomer pumping hardware was procured, interfaced to the computer/software system, and tested.

During FY 1992 (the final year of the project), a highly versatile vacuum metallizer was brought on line. Design is nearly complete for thin film deposition processing hardware to use in the machine.

The vacuum metallizer permits multilayer thin film coating of rolls of flexible substrate materials such as plastics, fabrics, screen, and metal foils. The modular design allows simultaneous deposition, with multiple sources, by the PML technique as well as by conventional vacuum deposition processes like sputtering, evaporation, and plasma polymerization. The substrates may be as wide as 6 inches and the length of material on a roll is related to the thickness: 6000 feet of 0.001-inch material can be used.

The system employs a pre-emptive multi-tasking data acquisition and control system that permits fully automated operation of the pumping, substrate motion, and deposition process systems. Fully manual and any combination of manual and automated operations are possible.

The substrate can be moved, back and forth, past the deposition zone at speeds as high as 500 feet per minute (±0.1% of set point). The lateral positioning of the substrate is controlled to ±0.003 inches. In a single pass, depending on the types of deposition sources in use, as many as seven layers may be deposited. More layers may be deposited by making multiple passes. For trial runs, 20-foot long closed loops of substrate material may be continuously rotated past the deposition zone.

No other existing facility permits the use of all of these coating processes simultaneously (and there is no other PML roll coating facility of any kind). This equipment will be invaluable in our development of energy conservation coatings and development of lithium polymer battery technology.
Fluid Dynamics Research

N. J. Lombardo (Applied Physics Center)

The objective of this project was to improve the scientific understanding of the behavior of complex fluids. Diverse processing areas such as chemical separations, material synthesis of separations materials, and physical separations were emphasized. The scope of the project included experimental investigations of phase interactions in multiphase flows, including turbulent slurries and physical separations of finely divided materials. Other activities included investigations to characterize the rheological properties of complex fluids; these characterizations are essential to predicting their flow behavior.

Multiphase Turbulence

Three experiments to investigate the fundamentals of multiphase particulate turbulence were initiated under this task. The first experiment is referred to as the multiphase HIT (homogeneous isotropic turbulence) experiment which is designed to provide data on the structure of turbulence and its decay rate in homogeneous isotropic flows. The second experiment involves study of free jets. The flow provides data describing turbulence generation and diffusion in regions of free shear and provides information on the effects of anisotropy. The third experiment, called the particle induced turbulence (PIT) experiment, provides data on turbulence generation caused by particles settling under gravity. This experiment is being conducted in collaboration with Washington State University.

All experiments have been designed to provide data of interest to modelers and analysts. The data of interest includes data describing: detailed velocity profiles, turbulence spectra and autocorrelations, turbulent kinetic energy, Reynolds stresses and higher order velocity cross-correlations, integral length and time scales, and velocity probability distribution functions for both the particle and fluid phases. Data will be used to evaluate a number of proposed models appearing in the literature. Analytical models and numerical codes developed both at PNL and at other research institutions will be evaluated using this data.

Currently, the HIT flow experiment is designed to provide data on solid-liquid flows; the jet experiment will investigate the flow of a pseudo-plastic fluid. In later investigations, the test fluids will be reversed. Accomplishments in support of the HIT experiment include the following: 1) a preliminary analysis was performed to ensure that data precision and quantity would be sufficient to provide a statistically accurate characterization of turbulence, 2) a test facility was designed and fabrication initiated, and 3) an index of refraction matched solid-liquid mixture was developed.

Calculations were performed to determine the test section dimensions, grid velocities, particle sizes, and measurement systems required to provide sufficiently accurate data to test theories appearing in the literature. A HIT flow test section with the appropriate geometry was designed and fabrication initiated. The design includes a special purpose traverse system to simultaneously move the optics and the grid with identical velocities. The measurement volume of the laser doppler anemometry (LDA) system is small enough to resolve spectral features.

The jet experiment has been designed and constructed. Shakedown tests have been completed. Testing with our recently developed particle image velocimetry (PIV) system will be initiated early in FY 1993.

The PIT experiment has been designed and is currently being fabricated. Equipment for image analysis of the falling particles has been procured.

An index of refraction matched mixture consisting of mineral oil, stoddard solvent (a dry cleaning fluid), and silica was developed for use in this experiment. Small quantities of this mixture were prepared and transparency to the green beam of an available Argon-Ion based LDA system was verified.

Although the current emphasis is experimental, the multiphase turbulence task also includes analytical and numerical efforts. FY 1992 activities consisted of 1) a literature survey to identify all the proposed two-phase
turbulence models appearing in the literature, 2) an evaluation of the ability of some published two-phase turbulence models to predict data, and 3) developing an ensemble average two-fluid model for dilute solid-liquid flows. The literature survey was used to identify the prevailing analytical and numerical methods to predict turbulent flow of particulate-laden mixtures. Because the papers also illustrate which quantities are of interest to the modelers, the information also supported the design for the various experimental test facilities. The shortcomings of two-phase turbulence models were identified during the evaluation of their predictive capabilities. Finally, application of ensemble averaging techniques provided a new method of obtaining rigorous turbulence models for particulate flows.

Non-Newtonian Fluid Dynamics Research

A comprehensive survey of the current literature was completed. The research ideas were refined as a result of collaboration and positive interaction with Professors R. B. Bird, L. G. Leal, R. L. Powell, and other active researchers in the area of non-Newtonian fluid dynamics. Some of the open non-Newtonian fluid dynamics research areas reviewed are: submerged pseudoplastic jets, bubble coalescence in non-Newtonian fluid dynamics, numerical solutions in viscoplastic fluids, turbulence in viscoelastic and viscoplastic fluids, and convective stability in non-Newtonian fluid mechanics.

On the experimental side, several types of activities have been completed: 1) development of appropriate working fluids, 2) study of pseudoplastic jets, and 3) study of viscoplastic fluids. Since PIV and LDA rely on the ability to transmit visible light through the flow field, the working fluids have to be optically transparent. A transparent working fluid for our viscoplastic studies has been developed. Preliminary tests with this mixture have shown that it is not birefringent. Viscometric measurements revealed that this fluid can be rheologically described by the Herschel-Bulkley model when under simple laminar steady shear flow.

An experimental setup has been designed and fabricated to study a turbulent pseudoplastic jet. The appropriate pseudoplastic fluid was identified to be a mixture of between 0.5% to 1.0% by mass of hydroxyethyl cellulose (HEC) and water. The instantaneous velocity distribution in the jet will be measured from which the turbulence characteristics of the jet will be resolved.

A preliminary qualitative experiment was also performed using a smaller setup to study the behavior of a viscoplastic jet. The results were compared to several numerical results obtained from existing codes at PNL that simulate the flow of purely viscous non-Newtonian fluids. The pseudoplastic and viscoplastic jets were observed to exhibit a much different qualitative behavior than their Newtonian counterpart. Additionally, the power law model was implemented and validated in an existing code at PNL to solve viscometric flows such as pipe flow and flow between parallel plates. The code was then used for (unvalidated) modeling of non-viscometric flows like two-dimensional driven cavity and free jet flows of pseudoplastic fluids.

Phase Separations

An extensive literature review was conducted in an attempt to identify cross-cutting hydrodynamic issues associated with the segregation of a dispersed solid phase in a liquid continuum. The outcome of this review indicated that 1) at the scale of interest to Advanced Processing Technology Initiative and the Hanford community, surface chemistry effects are significant and most likely dominate the hydrodynamics effects in a separations process, and 2) advances in phase separation technology is largely tied to enhancements of specific concepts or devices. Because no cross-cutting (i.e., across separations technologies) issues for research were identified, no further investments in this area are expected.

Rheological Modeling

An investigation of techniques to predict the rheology of suspensions was conducted. Techniques were identified that accounted for particle-particle and particle-fluid interactions. Attempts to reproduce results reported in the literature were made. Because of the long-term investment required to make progress in this area, this effort has been put on hold until further resources can be identified.

Advanced Instrumentation Development

A PIV system was developed for obtaining planar measurements of solid and liquid phase velocities in a
flow field. This state-of-the-art system will be supporting the turbulence and non-Newtonian flow studies and is an important tool for future research. Proposals were developed for two novel fluid measurement systems: acoustic holography for measurement of phase distribution and phase velocity, and a capacitance flow meter for measurement of flow regime, phase velocities, and film thickness in multiphase flows.
In Situ Monitoring of Ultra-Fine Particle to Particle Material Interactions

R. H. Jones (Materials Sciences)

The goal of this project is to understand and model the role of nanometer particle properties and particle-to-particle interactions on consolidation processes. The research included the characterization of nanometer particle properties, the interaction between ultra-fine particles, the comparison of these properties with micrometer-size particles and the in situ monitoring of properties during consolidation. The initial research emphasized nonmetallic nanometer particles.

Atomistic modeling of nanoparticle interactions was conducted for the following conditions:

• embedded atom modeling of the interaction between two 767-atom spherical clusters
• these clusters were annealed by assigning velocities to the atoms and allowing the assembly to equilibrate
• cluster pairs were annealed at 0K, 300K, 900K, and 1200K for up to 3 ps.
• the extent of cluster rotation and atomic rearrangements in the interface was studied.

The chemical (AES/XPS) characterization of iron oxide particles prepared by the reverse micelle process was completed.
Materials Synthesis

B. C. Bunker (Materials Sciences)

The goal of this project was to develop new synthetic techniques and/or new inorganic materials for ion exchange separations. Materials under development were to be used as both cation and anion exchanger, with the target cation being cesium and the target anion being the chromate ion. Work was centered on preparation of high surface area hydrous metal oxide powders such as iron oxide via techniques including aqueous precipitation, hydrothermal synthesis, synthesis in inverse micelles, and synthesis of ceramic ash via the glycine-nitrate process. An evaluation of current powders suggests that the most active, high surface area powders are too difficult to isolate and exhibit poor physical characteristics to function as optimum packing materials for ion exchange columns. Therefore, group efforts were focused on coating active hydrous oxide powders and gels onto ion exchange support media such as zeolites. The work directly supports the chosen reference inorganic ion exchanger, a titanate-coated zeolite developed at PNL, which simultaneously removes Cs, Sr, and Pu from radioactive waste streams.

Work during FY 1992 focused on preparing ultrafine particles via two techniques: the rapid thermal decomposition of precursors in aqueous solutions (RTDS), and synthesis in inverse micelles. The RTDS process has been used to prepare particles of zirconia, titania, and silicotitanates. X-ray and TEM analyses show that the particles are ultrafine (smaller than 10 nm), and are highly crystalline. The zeolite IE-96 has been coated with both titanates and silicotitanates prepared via RTDS processing. In the case of titanates, RTDS coatings yield ion exchange properties which are comparable to the titanate-coated zeolites prepared by a PNL researcher using titanium tetrachloride solutions. The silicotitanate-coated zeolite exhibits a selectivity for Cs which is ten times greater than the titanate-coated zeolites. The Cs selectivity of the silicotitanate-coated zeolite is significantly lower than that of another national laboratory best silicotitanates, in part because the zeolite core is less effective than the coating in adsorbing Cs. Finally, work this year has made significant progress in scaling up the RTDS hydrothermal process so that it can be used to make large batches of powder. The RTDS system is being used to evaluate processing conditions which will apply to the pilot-plant scale continuous hydrothermal equipment which PNL is obtaining.

Publications and Presentations


Process Engineering Science

E. O. Jones (Chemical Sciences)

Process engineering science is the key to the application and deployment of chemical and materials processing technologies, including advanced separations, catalysis research, biomimetic coatings, and organic destruction technologies. The objective of this project was to integrate process engineering science into materials synthesis and separation chemistry research related to separation technologies. Research in FY 1992 included scaling up a materials synthesis process, establishing capabilities in electrochemical separations, and testing inorganic ion exchangers for specific Hanford site applications.

The overall scope for FY 1992 was to develop advanced separations and material synthesis technologies. The initial integrated focus was on technology for cleanup of the Hanford site using inorganic ion exchange material directed toward a specific tank waste. In addition, technical expertise will be developed within the emerging technology of electrochemical separations. Ion exchange materials were prepared by materials scientists and chemists and tested in simulated Hanford tank solutions by process engineering science personnel. The ions of interest include radionuclides (especially Cs) and toxic metal cations and anions. These elements pose significant problems in industry and the DOE. Materials processes were further developed by building and testing novel engineering-scale materials processing equipment.

Inorganic Ion-Exchange Separations

Several novel ion exchange materials were evaluated with respect to Cs separation from simulated Hanford tank wastes. Cesium is a key radionuclide that must be separated from concentrated Hanford tank liquids prior to their disposal as low-level waste. The purpose of the testing was to identify promising materials that could be quickly and simply deployed in a compact process to solve an immediate separation need for the Hanford site. Ion exchange materials from other national laboratories (Sandia National Laboratory, Savannah River Laboratory, Pacific Northwest Laboratory), universities (Texas A&M), and private industry were evaluated in batch laboratory testing with simulated Hanford tank wastes containing tracer quantities of Cs. To be effective, these materials need to have a high selectivity in an environment with a Na/Cs ratio up to $10^5$ and good stability in solutions with greater than pH 13. In addition, the new materials would have to be consistently manufactured on a large scale. The most promising materials were an organic resorcinol-formaldehyde resin produced at SRL and crystalline silico-titanates at SNL. These materials are two to three orders of magnitude more selective than commercially available material. Both materials have high Cs selectivity at pH greater than 13 and could be used in a compact Cs separation process. The evaluation and testing performed in this project led to new opportunities for immediately removing Cs from Hanford tank waste and accelerating Hanford tank waste remediation.

Electrochemical Processes

Electrochemical processes have potential applications in several areas on the Hanford site and are an emerging technology for several industrial processes. Electrochemical processes investigated in this project included electrokinetic separations of Cs from soils, electrodialysis, electrochemical regeneration of ion exchange material, and electrochemical destruction of organics.

Electrokinetic separation of Cs from soils is an emerging environmental remediation technology that has potential application for other toxic metals. A plexiglas cell for the Cs tracer study was fabricated and a multichannel analyzer and ion probe were installed and calibrated. Preliminary experiments examined the effects of applied potential and soil moisture content. To support electrokinetic separations in soils, preliminary experiments with nonradioactive Cs were conducted to determine if the power supply had adequate voltage. Two constant voltage experiments were completed: one lasting 7 hours and another approximately 24 hours. Each showed significant movement of Cs ion in Hanford soil as 240 volts was applied to the cell. After the cold experiments, a radioactive Cs spike was added to clean Hanford soil. Total radioactivity was mapped as a function of
position within the cell. The resolution of the Ge gamma counter was not high enough to provide an accurate map of the Cs movement. Therefore, two new lead shields were constructed to increase the resolution and experiments will continue in the beginning of FY 1993.

Existing ion exchange processes typically use chemicals to regenerate the ion exchange materials which results in a secondary waste stream that creates storage and disposal problems. Electrochemical ion exchange increases the process rate by application of a voltage gradient which allows the ion exchange materials to be loaded more efficiently. The process also reduces the amount of secondary waste produced by generating H⁺ ions in situ for elution of the Cs. An electrochemical ion exchange cell was constructed and approximately 200 grams of Cs-100 ion exchange material was obtained for testing.

Electrodialysis is particularly effective in separating mixed wastes because it reduces the secondary waste generated during processing. A single membrane micro-cell was constructed and the Nafion 417 membrane was used to evaluate the ion mobility of Cs in a solution of NaNO₃ with a Na/Cs molar ratio of 1000.

To support organic destruction in Hanford tank waste, an investigation has begun to determine the oxygen overpotential of several novel metals. A high O₂ overpotential is preferred for electrochemical organic destruction to minimize the current passed to O₂ evolution. Cyclic voltametry will be used to evaluate the O₂ overpotential. A cell was cleaned and set up for preliminary experiments with a Pt electrode. Other metals that will be characterized are: SnO₂, SnO₂ doped with Sb, Ebonex. and In₂O₃.
Separation Chemistry

R. T. Hallen (Chemical Sciences)

This project focused on research efforts to discover new or improved separations of importance to the DOE mission at Hanford. The objective was to integrate the Laboratory strengths in fundamental research with the applied chemistry and engineering activities related to separation process development. Research was performed to better understand chemical separations and develop separation technologies based upon a fundamental understanding of ion exchange theory. The scope involved developing advanced separation technologies for cleanup of the Hanford site. The main focus was on the evaluation of inorganic ion exchangers. Target cations for the separations included cesium, strontium, and plutonium. Of most importance was the development of improved materials and processes for cesium removal. A titaniu-coated zeolite developed as PNL, IONSIV TIE-96, was chosen as a reference material for comparison. Other exchangers having greater selectivity and capacity for cesium ion separation were investigated. Of specific interest was the development of hybrid ion exchangers such as a zeolite with nickel ferrocyanide or organic-ligand-modified silica gel. Alternate processing schemes were also explored. Membrane separations have the potential to reduce secondary waste generation compared with the regeneration of ion exchange columns. Membrane research was directed at the development of surfactants for biomimetic membranes and the synthesis of functionalized, water-soluble polymers for ultrafiltration.

Modified Zeolite Exchangers

Sodium nickel ferrocyanide [Na$_2$NiFe(CN)$_6$] is known to have a high affinity for the selective ion exchange of cesium ions. It has been used extensively for this purpose for the removal of radiocesium from the supernate of high-level waste tanks at Hanford. Four zeolites were initially chosen for loading with nickel ferrocyanide. They are IE-96, copper-mordenite, silver-mordenite, and lead-faujasite. The zeolites were loaded by stirring with a saturated Na$_2$Fe(CN)$_6$ solution then contacted with NiSO$_4$ to precipitate Na$_2$NiFe(CN)$_6$. To increase the amount of Na$_2$NiFe(CN)$_6$ loaded on the zeolite, the solids were exposed to a total of seven cycles of NiSO$_4$-Na$_2$Fe(CN)$_6$-drying treatments. Samples of the zeolites were taken after each cycle to be tested for cesium uptake ability by batch distribution. Samples of the zeolites were also analyzed to determine the amount of ferrocyanide adsorbed on the surface of the zeolite using FTIR spectroscopy.

The various nickel ferrocyanide-loaded zeolites were batch contacted with a West Valley synthetic waste supernate to determine relative distribution factors, $K_d$, for cesium. The results showed that $K_d$ could be increased by multiple cycles of ferrocyanide precipitation. In general, the $K_d$ increases by a factor of 3, reaching maximum selectivity for materials with 3 to 5 loadings.

The trend in the batch distribution showed a major difference in the $K_d$ values for lead-faujasite compared with the mordenites and IE-96. The mordenites and IE-96 showed much higher $K_d$ values for Cs than was observed for the faujasite. Differences in $K_d$ can be rationalized in terms of the relative surface areas of these zeolites. The mordenites and IE-96 have a much higher surface area per gram of material than the faujasite zeolite. The uneven and highly porous surface of the mordenites and IE-96 allows for higher adsorption of the nickel ferrocyanide ion exchange material at the surface. In contrast, the faujasite has a very regular surface and is formed as a spherical bead. The surface-to-volume ratio for this geometry is at a minimum and, therefore, the amount of ferrocyanide that can be adsorbed to the surface is minimized.

The surface infrared spectra of the coated zeolites were obtained to demonstrate that the ferrocyanide is attached to the surface of the zeolites. The relative absorbance at 2080 cm$^{-1}$ (the IR region diagnostic for nickel ferrocyanide, $\nu$ C=N) was determined for a series of NiSO$_4$-Na$_2$Fe(CN)$_6$ loaded zeolites and for solid Na$_2$NiFe(CN)$_6$. The absorbance of the ferrocyanide-active band in the loaded zeolites is in the same location as for the pure Na$_2$NiFe(CN)$_6$ solid material, which indicates that the coating material is similar to the pure sodium nickel ferrocyanide.
Silica-Based Hybrid Exchangers

For cesium sequestration by hybrid materials, pseudocalixarene surfaces have been targeted due to the high cesium affinity of the calixarenes. Since the phenol/silica condensation route to functionalize both silica and alumina surfaces has proven successful, attempts were made to bind hydroquinone. Volatility problems prevented this reaction from occurring. Attempts to circumvent this problem included increasing the molecular weight and the acidity of the organic species. Three modified phenols were successfully attached to silica and alumina. However, two of the compounds appeared to bind at both ends, thereby eliminating the utility of these systems as calixarene mimics. This molecular arrangement may prove beneficial in the future for subsequent surface derivatization (e.g., molecular attachment via imine formation at the benzophenone carbonyl), but will not be studied further at this point. The readily prepared 4,4'-biphenol derivative appears to have a great deal of promise as a calixarene mimic. The high surface area of this substrate (Cab-O-Sil; 150 m²/g) should make it ideal for batch extraction. This material will be characterized by solid state ¹³C CP-MAS NMR and FTIR. Once this material is characterized, it will be tested for cesium uptake by batch distribution.

An alternate method for silica surface modification by attachment of organic complexants was also explored. Conversion of surface silanol groups to trifluorooacetate groups by reaction with trifluoroacetic anhydride is being investigated. IR and ¹³F NMR spectroscopies suggest that the surface of Cab-O-Sil are modified in this way. Trifluoroacetate should be a better leaving group than hydroxyl. If displacement with nucleophiles is favorable, this would be a general route for organic attachment.

The attachment of CMPO (the TRUEX extractant) to silica was targeted for removal of americium and plutonium. The synthesis of phosphine oxide analogs of CMPO has been improved so as to minimize the formation of the undesired side product. Once the compounds are adsorbed onto a suitable substrate (i.e., silica), thermally induced condensation of the alcohols to the surface will covalently attach the molecule to the substrate. This method has been explored using phenolic model systems and found to be a viable approach within certain limitations.

Ultimately, this will provide two alternate approaches to CMPO analog derivatized surfaces. Long chain alkyl groups have been attached via this method which have application in biomimetic membrane separations (vesicle extraction).

Another route to silica-bound CMPO was pursued with Dr. Richard Hammen of Chromatochem, Inc. A cost-shared proposal for development of silica-based ion exchange materials has been prepared and research is progressing. Chromatochem manufactures selective exchangers for separation of metal ion from aqueous solution. PNL will evaluate the materials for nuclear applications.

Membrane Separations

PNL collaborated with Professor Hal Monbouquette (UCLA) on the use of biomimetic membranes for selective separations. PNL's task was to synthesize inexpensive surfactants to replace the costly natural compounds currently being used. Professor Monbouquette has reported that the surfactant we supplied him will form vesicles that absorb metal ions in water. The surfactant is deficient in regard to the thermodynamic stability of the vesicles it forms. The vesicles degrade in time to a lamellar phase. Naturally occurring, vesicle-forming surfactants have longer tails and larger zwitterionic head groups than the alkylbenzene sulfonate surfactant we prepared.

Modification of the vesicles by addition of single-tailed, long-chain cosurfactants is being pursued by Monbouquette. We are developing alternative surfactants that might better mimic the naturally occurring physical size and charge requirements. Monbouquette has received notice that he will be awarded a 2-year NSF grant to continue development of this technology. He looks forward to a continued, if not expanded, collaboration with PNL.

The application of ultrafiltration technology was also explored. Ultrafiltration was evaluated in conjunction with water-soluble polymers as separating agents. Five copolymers were prepared which contained acrylic acid and polyethylene glycol acrylates. Low-molecular-weight polyethylene glycols have been shown to have chelation properties similar to those of crown ethers. These copolymers are currently being examined for complexation of europium ion, a substitute for americium. The copolymers are also
being characterized for average molecular weight and amount of acrylic acid present in each polymeric chain. Preliminary work has shown the polymer to be 15,000 mw and excluded by ultrafiltration membranes with cutoffs of 1,000 and 10,000 mw. This research is in collaboration with Professor Francis DiGiano from the University of North Carolina at Chapel Hill.
1.3 Energy Distribution and Utilization
Application of AI Technology to Power Plant Operations and Maintenance

D. B. Jarrell (Nuclear Systems and Concepts)

This project was aimed at developing an effective approach to the identification, analysis, and solution of power plant operations and maintenance problems. This approach involves assessment of plant infrastructure functionality, improvement of element cost-benefit, plant-specific implementation development, and operator interface training.

Prototype Advances

The basic vehicle for demonstrating the Model Based Reasoning (MBR) technology that underlies the Decision Support for Operations and Maintenance (DSOM) diagnostics is the Root Cause Analysis Research (RCAR) computer prototype. This prototype was constructed in 1990 - 1991 using PNL LDRD funding and has been integral to demonstrating the future capabilities of the DSOM system. The RCAR demonstrates the ability of the model-based reasoner to display to the user the failure mode (type of failure [i.e., leak, block, or heat transfer degradation]) based on the process indication parameters (temperature change, mass flow) for a typical shell and tube heat exchanger (HX).

To achieve a demonstrable product within the existing research budget, it was necessary to severely limit the faults that the user could input to the original (FY 1991) HX simulator module. One fundamental failure that could not be included in this original work was the ability to show the effects and solution (diagnosis) of an inter-fluid (primary to secondary) leak.

Modeling the effects of an inter-fluid leak required that the simulator module be extended beyond the existing boundary of the basic HX to include the secondary (cooled fluid) expansion tank. In FY 1992 the equations that govern the physical phenomena involved were properly assembled, programmed, and integrated into the HX simulator model. This effort required considerably more time than planned, consuming the funding allotted to this task.

Considerable competition for existing research funding did not allow allocation of additional funds to complete the integration of this task into the operating prototype.

Computer Aided Site Assessment

The CASA system is a computer software approach to automating much of the time-consuming processes required to accomplish a (plant) performance assessment. If developed, CASA offers a 50% cost reduction in an assessment process that is essential to understanding the effectiveness of most of our large industries (e.g., nuclear power, DOE and DOD facilities, public education, etc.).

In FY 1992, the steps and procedures incorporated in a plant performance assessment were described in detail. Based on this description, a methodology and framework for developing the CASA system was derived.

Maintenance Optimization

The DSOM system makes performance information available at a level that previously was available only to processes that were highly sensitive to economic or risk dominant factors. Accurate utilization of this detailed information to make accurate operations and maintenance decisions requires analytical resources that are beyond the capability of most facilities. Following the diagnosis of a declining or faulted process, a method for evaluating the alternative courses of action must be evaluated on a cost or risk basis. The methodology developed in this task can be adapted to the DSOM hardware that will perform and display the optimum action based on the user's requirements. The technique has the potential to be transparently embedded in DSOM to produce optimum operations and maintenance alternative selections.

The Aging Management Optimization Software (AMOS) was originally designed to perform circuit
feedback analysis in the electronics industry. It was realized that the basic program provides the feedback logic and characteristics to model a multi-path decision tree. Through this task, we have modified the original program to accept as input the data structures from diagnostic information similar to DSOM. The feedback loops are then treated as process decision modifiers allowing iterative alternatives to be examined. While the output from the program is not yet compatible with DSOM format, it will allow a graphical comparison of alternatives with a base case datum.

Publications

Chemical Process Efficiency

R. S. Butner (Chemical Sciences)

Applications in materials fabrication, chemical processing, fuels, and environmental control technology were pursued with the singular goal of developing the knowledge, tools, and capabilities required to expedite the reaction engineering process. Research and development was conducted in the area of chemical reaction engineering, particularly multiphase reaction systems. The project was intended to lead to both conceptual "breakthrough" technology, as well as significant improvement in the selectivity and yield of conventional processes.

Dehydrogenation Reactions

Commercial palladium membranes are available that are permeable to hydrogen and much less permeable for other gases. By placing one of these membranes in a reactor, it is possible to remove hydrogen, continuously as it is generated from dehydrogenation reactions. Steam-methane reforming, a reaction widely used in industry to generate hydrogen, was chosen to demonstrate this membrane reactor concept. At typical operating conditions, the reaction of methane with steam to produce hydrogen and carbon monoxide is limited by equilibrium to about 50 to 60% conversion and the product gas contains H₂, CO₂, CO, and unreacted CH₄. During FY 1992, a laboratory-scale membrane reactor was assembled and tested for methane reforming. The reactor consisted of a 0.75-in. Inconel tube with a 0.25-in. Pd-Ag tube inserted down the center of the reactor tube. By continuously withdrawing H₂ through the Pd-Ag membrane during the course of the reaction, we were able to achieve over 90% conversion of CH₄ in a single step. Two gas streams were produced, one contained essentially pure H₂, the other contained primarily CO₂ and the small amount of unreacted CH₄. Additional data will be generated with this reactor system in FY 1993 which will lead to publication of the results.

Solid Acid Catalysis

During FY 1992, the Grade V Scientists Project on Advanced Catalysis produced several novel acid catalyst materials and will continue to do so during FY 1993. Working with Dr. Bill Thompson of Washington State University, Chemical Engineering Department, we identified alkylation as an important reaction in the petroleum industry where a membrane reactor would be highly desirable for implementation of solid acids in this process which currently used liquid acids. Developing a membrane-reactor concept for alkylation will be one of the goals of FY 1993 research activities.
Development of Advanced Flow Cytometry Methods for Investigating EMF-Induced Calcium Ion Mobility

J. E. Morris (Biology and Chemistry)

Recently acquired flow cytometry instrumentation provides a unique capability to investigate cellular mechanisms involved in electric and magnetic field effects on biological tissue. This project resulted in direct interfacing of magnetic field exposure systems to the cytometer, and helped to enhance the technical ability to carry out detailed mechanistic studies on effects of environmental agents at the cellular level.

Three of the four major objectives of the project have been realized. These include design, fabrication, and testing of an in vitro exposure and sampling system; interfacing of the sampling system with the fluidics of the flow cytometer; and establishing methods of acquiring and storing the data sets generated during the 1-hour exposure periods. The additional work element required is the acquisition of calcium levels during different EMF exposures and frequencies.

The design specifications of the in vitro exposure and sampling system included the ability to control sample temperature within a few tenths of a degree centigrade using a water jacket, to use with a solenoid magnetic field exposure chamber and to permit the acquisition of samples using the fluidics of the flow cytometer.

Interfacing the sampling system with the fluidics of the flow cytometer resulted in the ability to measure, in near real time, cytoplasmic free calcium levels in cells during exposure to magnetic fields and also provided a method for the detailed investigation of signal transduction using calcium ion levels. The data acquisition and storage system developed in the project will allow for the retention of large data sets for additional analysis and evaluation.
Diagnostics and Controls

M. R. Bramble (Energy Sciences)

Field investigations conducted by PNL have shown that poor design, installation, operation, and maintenance of energy systems can be major causes of wasted energy. This project consisted of identifying the root cause of operating and maintenance problems followed by the development of advanced technology to mitigate these problems in the buildings, facilities, industry, and utility sectors. Initially, technology development focused on further developing state-of-the-art automated model-based diagnostic systems and on developing sensors that require little or no calibration.

The no-fault prototype of a model-based diagnostic system was completed in FY 1992. This prototype demonstrates automated diagnostic capabilities during normal operation of a rooftop heating, ventilating, and air conditioning unit that has no degradation or faults in the damper subsystem. An enhancement to the no-fault prototype, the selected-faults prototype, was 90% completed during FY 1992. The selected-faults prototype extends the no-fault diagnostician to provide results for a selected set of simulated damper faults.

The approach under development uses model-based reasoning, in which an integrated set of heterogeneous information models and the ability to reason about them are embedded in software. This approach ultimately will provide diagnostic systems the ability to automatically detect and diagnose problems not anticipated a priori by the developer of the diagnostic systems. The prototypes under development in this effort are hand crafted; one of the major challenges for the future will be to develop methods and tools to automate parts of the process of designing and building model-based diagnostic systems.

A discrepancy analyzer, which is a key component of the reasoner, was 95% complete in FY 1992. It determines if discrepancies (i.e., differences) exist between expected values and actual values of a set of variables, where expected values are determined from relationships developed from fundamental physical principles. When a discrepancy is detected, a fault has occurred in the system being diagnosed. Discrepancies between actual and expected state variable vectors will be used later to distinguish between the possible causes of a fault.

A considerable fraction of the prototype development effort was devoted to developing a generic diagnostic software system infrastructure (SSI), which provides communication and control between multiple software processes. A workable SSI was developed for the prototypes, and development of the generic SSI was 40% complete at the end of FY 1992.

Development of the no-fault and selected-faults prototypes comprised approximately 40% of the total project effort. Other parts of the effort focused on extracting models from field data and identifying and characterizing field performance problems with potential for application of automated diagnostics.

Other tasks focused on compilation of operations and maintenance problems found in the field; developing methods for screening actual end-use energy consumption data to identify operation problems in buildings and for extracting physically meaningful models from the data, which could then be used as the basis for automated diagnostics and to determine the energy impacts of operations and maintenance problems; and an examination of impacts of operations and maintenance problems using computer simulation.

The summary of building operations and maintenance problems was compiled from a large set of notes and experiences collected during field work. The data base contains a list of reported building operations and maintenance problems and contacts for each. The list contains observations of building managers at the ELCAP/REMP commercial buildings in Seattle and other locations throughout the Northwest, as well as PNL staff during work at military installations throughout the country.

For industrial applications of automated diagnostics, a review of options for self-calibrating sensors was completed. Results showed that self-calibrating sensors are not currently available.
A review of potential applications of microtechnology for industrial operations and maintenance was also completed, showing significant potential for future application to energy systems.

Presentation

Laser Energy Receivers

N. C. Anheier (Energy Sciences)

This project is a continuation of the investigation of monochromatic photovoltaic converters as laser energy receivers for space power transmission systems. Primary activities included further modeling, fabrication, and characterization of cells in an attempt to achieve single-cell efficiencies in excess of 70% monochromatic energy conversion efficiency. Efforts are aimed at overcoming panel design problems arising from the nonuniform delivered by a laser source. Development of wave guide analysis software, design, and fabrication of prototypic wave guides, and laboratory testing to determine the amount of uniformity was achieved. The last activity involved developing receiver array models and validating the model calculations through laboratory experiments with prototypic subarray elements and simulated laser transmitter jitter and beam non-uniformities.

In FY 1992, the power beaming testbed was upgraded with a volumetric disc power meter used to calibrate the optical power reaching the cell under test. Copper calibration apertures were fabricated and coated with gold. These apertures allow measurement of the optical power passing through known areas (i.e., 0.25, 0.5, 0.75, and 1.0 cm² [all circular areas]). Also a special aperture (4*20 mm rectangular) has been fabricated. This aperture closely resembles the typical dimensions of AlGaAs photovoltaic cells, developed by our university collaborator on this project. This effort is aimed at improving the validation of efficiency estimates for the cells.

The modeling software, which generates the laser intensity profile at the receiver after the beam travels through the integrator, was revised. The software package, SpyGlass, was examined for use in visualizing raw data. SpyGlass allows importation of the data and three-dimensional plotting. Also, sequential data generations can be plotted and linked together with an animation technique so that an evolving phenomenon can be visualized. The revised model will allow the investigator to visualize the effect of laser jitter on the intensity profile (among other things).
Magnetic Shielding Materials

J. D. Affinito (Materials Sciences)

This project demonstrated processes by which thin film composite magnetic shielding materials could be used to attenuate leakage fields from small electronic devices, including certain home appliances. Vacuum-deposited high permeability metal coatings were produced and studied with regard to their low frequency magnetic field shielding properties. The shielding was accomplished by optimizing magnetic parameters of sputtered metals, as well as the properties of substrates.

In FY 1992, low frequency magnetic field shielding materials were produced during three separate experiments in vacuum deposition chambers in the Research Technology Laboratory. Materials from these runs demonstrated the flexibility and interlayer adhesion properties required for successful shielding. Layered materials have been produced using both Permalloy 78 and μ-metal as target materials. In the last of the three runs, the spinning magnet array was installed in an attempt to control isotropy and thus achieve the needed magnetic properties without annealing. This run was only partially successful because a bearing on the spinning magnet array overheated and caused the magnets to remain stationary during most of the deposition process. This experiment will need to be repeated in order to continue development of these materials. To eliminate the problem in the future, a pair of Helmholtz coils will be designed and installed so that the required rotating magnetic field can be produced by driving the coils with an ac signal having a constant phase difference between the two coils.

For testing and performance evaluation of the materials produced in this project, a small portable square Helmholtz coil pair was designed and fabricated. It is used in conjunction with a Bell Gaussmeter and μ-metal and copper cylinder standards for determining the relative shielding effectiveness of the newly fabricated materials.

Materials produced so far, exhibit shielding properties at low field strengths; however, their performance is not sufficient to supplant μ-metal for most applications. Proper control of the magnetic field near the web during deposition will allow the production of materials having the required magnetic isotropy properties and thus exhibit shielding performance superior to that of μ-metal. Spreadsheet calculations using empirically derived equations for field attenuation clearly show that the layered configurations can outperform single shell configurations for materials having the same magnetic properties.

The effort to develop magnetic shielding materials has recently gained attention outside of PNL. Efforts to develop these materials are featured in an edition of USA Weekend, published on January 3.

Tennessee Valley Authority has expressed interest, and a proposal to develop materials for their specific needs has been submitted.

EPRI, several utilities, and Dominion (a technology investment group that seeks opportunities in energy-related technologies for the investment of electrical utility funds) have also expressed interest in the technology.

The technology is directly applicable to the goals and missions of DOE-CE, Utility Technologies Program, however, no formal proposals have yet been developed.
Power System Dynamic Analysis

D. J. Trudnowski (Energy Sciences)

New expertise and concepts for power system analysis and control system design were developed. The scope for this project included: power system analysis techniques such as power flow, transient simulation, eigenanalysis, signal analysis, frequency-domain analysis; control system design techniques that may be used for system stabilization; and investigation of totally new analysis techniques.

A major accomplishment of this project was the development of the computer program IPRONYID. IPRONYID uses Prony analysis to estimate transfer functions from dynamic system time-domain data obtained by conducting field tests. Basic algorithms were developed and coupled with routines from similar Bonneville Power Administration (BPA) analysis codes. BPA and the U.S. Bureau of Reclamation has shown considerable interest in using the programs for power system applications. Also, the program has been used for modeling and control system development of prototype robotic systems for waste tank restoration. Results related to this work have been used as the basis for three recent professional publication submissions.

The second major achievement involves development and testing of fundamental algorithms for fitting transfer functions to the frequency response of a dynamic system. In many power system field tests, such data is obtained, but adequate methods of analyzing the data have not been developed. Standard methods of fitting such data to a dynamic model are very numerically sensitive; therefore, a new approach has been tested which uses frequency normalization and transformations of the transfer-function model so that it is represented by a ratio of Chebyshev polynomials. Initial tests of the new approach are very promising.

The last two areas involve the computer visualization of transient stability simulation data in real-time and the parallel eigenanalysis of large matrices. With the visualization, the system is represented as a one-line diagram with various "moving" components. Significant computational speed-ups were obtained in parallel QR algorithm for performing the eigenanalysis problem.

Publications


Transportation Materials

G. L. McVay (Materials Sciences)

Lightweight transportation materials, advanced materials processing technologies, and integrated sensor and control devices are required by the automotive transportation industries to meet national energy, safety, and environmental goals. This project was directed at developing new knowledge and technologies to address transportation materials problems. LDRD-funded efforts to support this goal included development and demonstration of unique wear- and corrosion-resistant coatings, development of advanced optical coating processes for automotive applications, and demonstration of PNL sensor and nondestructive examination (NDE) technologies for automotive applications.

New techniques and concepts were developed to support a demonstrated application of superplastic forming (SPF) technology through prototype forming of a GM Electric Vehicle Battery Tray. Success from this effort has led to selection of additional components for demonstration.

Baseline superplastic properties and processing parameters were established for aluminum Al5083 alloy through collaborative PNL/university research efforts. Two- and three-dimensional modeling simulation and predictive capabilities were developed utilizing the commercial MARC analysis code. These capabilities were used to simulate the forming process for the Electric Vehicle Battery Tray.

Advanced multilayer polymer coatings were applied to automotive-type windshield glass to demonstrate low-cost thermal management techniques.

A conceptual approach was developed and proof of principle demonstrated for an advanced multilayer lithium/polymer battery.

Proof of principle was obtained for variable reinforcement Metal Matrix Composite (MMC) tube extrusion.

An optical-based hydrocarbon sensor was developed for application to automotive emissions and combustion control systems. Sensor performance was evaluated and other DOE/industry applications were analyzed.
Ultralight Fabric Radiator Development

R. J. Guenther (Nuclear Systems and Materials)

The objective of this project was to demonstrate the feasibility of fabricating an ultralight heat pipe for thermal management applications in space. This was accomplished by fabricating two ultralight heat pipes using copper liners with ceramic fabric overwrap.

The focus of this effort during the last 2 years has been on ultralight fabric heat pipes that could be used in heat rejection systems to produce significant system mass reductions and high survivability in both natural and hostile environments. This is significant because thermal management subsystems are often up to 50% of the total system mass. The ceramic fabric is ideal for radiator applications because of its high emissivity (0.93) and low absorptivity (0.10) in the solar spectrum, protection from damage by hypervelocity impact of micrometeoroids, as well as structural support to the very thin liner. These radiator designs have focused on the removal of waste heat from various space systems, including the SP-100 and multi-megawatt nuclear reactor concepts, lunar colony habitat and construction, nuclear electric propulsion systems, and others. Potential terrestrial applications for the technology to produce very thin liners include use in airplanes and chemical/food processing.

Activities during the previous year focused on the development of the UNITUBE process to cold form the liner, and on a method for attaching the ceramic fabric to the liner. The process parameters were developed to fabricate liners with wall thicknesses as thin as 0.0015 inch and lengths up to 51 inches; materials evaluated included copper, titanium and niobium-1% zirconium. This process allows the fabrication of liners with very thin evaporator regions (0.0015 inch) and thicker ends (0.020 inch) from the same starting material. Pressure tests on the copper liners indicated that the significant cold working that occurred during the fabrication process resulted in low ductility. A variety of options were explored for fabric attachment: brazing, mechanical swaging, and pulsed magnetic swaging. A mechanical swaging method using a copper collar was chosen for attaching the fabric.

Based on the previous year's results, activities in FY 1992 were focused on developing an annealing process for the copper liners to improve their ductility, finalizing the enhanced attachment technique, completing additional modifications to the UNITUBE equipment, and incorporating these fabrication improvements into two copper heat pipes.

All of the current objectives were met during the year. An annealing process was developed for the copper liners to remove the extensive cold working; pressure tests indicated the improved ductility in the copper liner. A technique for attaching the ceramic fabric to the thicker ends of the liner was refined and modifications and improvements were made to the UNITUBE process equipment. Two ultralight ceramic-fabric heat pipes were successfully fabricated with copper liners with ultrathin walls (0.002 inch). Silicon carbide (SiC) ceramic fabric was placed over the liner and attached at the thicker ends of the liner that were closed using soldered end caps.

A display was prepared for the Space Nuclear Power System Symposium in Albuquerque, New Mexico, to emphasize the ultralight fabric heat pipe concept. Key individuals from NASA, Phillips Lab (USAF), and DOE attended and meetings with the representatives were arranged to discuss future funding of the work on ultralight fabric heat pipes.
Visualization of Energy and Power Systems Data

D. R. Jones and M. W. White (Computational Sciences)

Developing new capabilities to support the visualization of energy and power transmission system data was the focus of the LDRD activity. This project was limited to the visualization and data management in support of visualization of electromagnetic fields (scientific data), power systems planning models (economic and business data, characterized by a large number of variables, and massive amounts of data which are generated by multiple iterations of the models as they try to achieve optimization), end-use metering data (massive amounts of multifaceted data with the inherent need for visualization to support information extraction), and visualization of real-time power systems models (scientific data).

This project was designed to develop new and enhance existing expertise and understanding of energy and power systems data and the use of visualization techniques for presenting and analyzing that data.

The AVS software was our initial visualization tool for prototyping and demonstration purposes. It was our intent to utilize energy and power systems data that currently exist at PNL. While much of this data related to specific programs or applications, they will suffice to develop generic visualization tools, and will certainly suffice to broaden the team’s understanding of the visualization issues involved. The range of visualization techniques which were investigated included, but were not limited to, AVS and AVS-type tools, multimedia presentation, linking database and image retrieval within a single RDBMS, and animation.

During FY 1992, a new method for visualizing power system data in real time and a sample video tape of visualization of three cases of power system disturbances were produced, and real-time data display using symbols and layout familiar to power system engineers was developed.
1.4 Other Lab-Level Projects
International Germanium Experiment

R. L. Brodzinski (Materials Sciences)

The objective of this project is to produce and operate several of our ultralow-level background germanium spectrometers utilizing 20 kg of enriched Soviet germanium, to set the world standards on lepton nonconservation, neutrino mass, and grand unification, and to develop technology for making radiological measurements on environmental samples. The measurement technology will provide significant cost savings over currently available technology and will have applications on samples of interest to the national security of the United States.

Three 1-kg detectors have been fabricated from 5 kg of enriched $^{76}$Ge supplied to us by the Soviet Union. An additional 15 kg of enriched $^{76}$Ge has been received from our Russian colleagues, and this material has been reduced to metal, purified, and is awaiting transformation into detector-grade crystals at Oxford industries as soon as they perfect the art of growing very large crystals. We have made the first confirmed measurement of the two-neutrino double-beta decay of $^{76}$Ge and the first measurement of the double-beta decay of $^{100}$Mo to the excited states of $^{100}$Ru. We have been invited to give 17 talks at international symposia, and we have written 24 peer-reviewed publications. Significant improvements in the experimental protocols have been achieved by adding research teams from the Soviet Institute for Theoretical and Experimental Physics and the Yerevan Physical Institute to the collaboration.

Further understanding of the source and nature of radioactive background has been obtained from our experimental facility in the Homestake mine in South Dakota. Improvements have been made to our experimental facility in Canfranc, Spain, to ready it for the long duration data acquisition program anticipated following detector fabrication and testing in Homestake.

Part of our objective is to test potential sources for the missing mass of the universe. Possible sources receiving major attention by theorists currently include WIMPs (Weakly Interacting Massive Particles) and MACHOs (Massive Astrophysical Compact Halo Objects). We have developed a technique looking for diurnal modulations in interaction rate data between dark matter components in the galactic halo and our detectors. The premise is the rate will decrease when our detectors are on the "downwind" side of our earth’s motion through the galaxy due to additional attenuation by the thickness of earth traversed by the particles before reaching the detector. A glance at a globe will show this effect would be greatest for detectors located in the southern hemisphere. Correspondingly, we have been contacted by representatives from the University of Buenos Aires and the Argentine government with the desire to establish one of our low-background laboratories in their country. Plans to do so are in progress.

Some noteworthy facts that demonstrate the importance, prestige, and sensitivity of these experiments include the following:

- The value of the total 20 kg of enriched $^{76}$Ge being provided by the Soviets is on the order of $30$ million.

- The international collaboration has now expanded to South America in addition to Europe.

- The radioactive background in a 2000-year-old Roman lead sample sent to us via air freight by our Spanish colleagues was dominated by radionuclides induced by cosmic ray interactions incident on the lead at the high altitude of the flight.

- A copper shield electroformed in Richland to eliminate all background radioactivities was sent via a commercial bus service immediately after electroforming to our facility in South Dakota to avoid the high altitude cosmic ray flux--the background was still dominated by radionuclides produced by cosmic ray interactions during the bus ride.

We expect to set the world standard on lepton nonconservation, neutrino mass, and grand unification by 1995.
Publications


Presentations


Vertical Integration of Science, Technology, and Applications (VISTA)

G. B. Morgan (Computational Sciences)

The goal of this project included completing a technical and user needs assessment of the VISTA software system, which was previously developed to provide broad network-based access to computer resources and computational programs that were not designed for modern computing environments. Thus, successful development of VISTA would allow the quick development of custom applications used in solving the complex DOE problems in the area of waste management and environmental restoration. The objective for the assessment is to evaluate the progress on the VISTA project to date.

The assessment process was divided into three major activities: 1) technical assessment of the software developed (to date), 2) user needs, and 3) maintaining an active capability.

Technical Assessment of the Software Developed To Date

This task was conducted in collaboration with Battelle Columbus Laboratories. The technical assessment consisted of evaluating the following elements:

- quality of code for the purpose of this assessment, quality of code was defined to be correctness (judged by its conformance to its defined functionality); completeness (if it implemented all planned functions); openness (coded in conformance with ANSI C standards); and portability (if it met certain criteria with respect to projected target platforms)

- configuration and release control
- system and user documentation
- planned versus implemented functionality
- maintainability.

Areas in which deficiencies were found were in documentation, configuration control and release management, performance goals, testing, and the use of standard subsystem development methodologies. These are all areas that were recognized in July 1991, but were not pursued to completion because of the budget cutback and the priority of the ADE development at that time.

Documentation is an area in which standardization is needed. There appears to be no common methodology for documenting the system, making it difficult to understand how the system functions. This is an area in which improvement is necessary.

Configuration control and release management have been used extensively in the VISTA project to date but will become increasingly important if the VISTA software moves into a production phase. The VISTA development team already has the tools to implement a good system for controlling the software. All that needs to be done is to use them.

Performance goals were not formally addressed in the original VISTA design. At VISTA’s level of maturity, now is the time to consider these requirements.

Past test practices in VISTA have delegated test methods and processes largely to the discretion of the subsystem developers. This has worked acceptably well during VISTA’s development stages. To ensure that VISTA is a robust product, however, the project must implement more uniform test procedures.

Development methodologies within subsystems has largely been left to the discretion of the subsystem teams. The use of uniform and consistent methods and tools across subsystems would enhance the VISTA product and is essential to controlling maintenance costs.

The net finding from the technical assessment activities was that the VISTA software can be considered to be a very good prototype but needs additional work to be directly applied to scientific and technical programs. VISTA was rated highly in terms of design concept and modularity. This is perhaps its strongest
asset. As a result of this modularity, each of the subsystems can be used individually or in combination with other subsystems in projects that require their specific capabilities.

This modularity is most apparent in the decomposition of VISTA into subsystems. It is also true of the subsystem decomposition into modules and C functions. While there are some large modules, the majority of those examined are small, regular, and manageable.

An innovative aspect found in the software was the message set: a defacto integration specification which allows the VISTA subsystems to coordinate activities. While not a formal part of the original design specifications, it plays a key role in the system. It is recommended that the message set be further defined and given more prominence as the official integration specification. This is sometimes referred to as the "framework" and is one of the strongest aspects of the system.

User Needs

The second major element of this assessment was to evaluate the needs of potential scientific and technical users of VISTA. Areas of the user needs evaluation included:

- Identification of commercial and governmental software and tools similar to VISTA
- Evaluation of the claimed functionality compared with VISTA
- Identification of potential strategic partners to fill gaps identified
- Evaluation of the impact of VISTA on future PNL program mission requirements
- Determination of the best method for PNL to use VISTA technology in meeting DOE needs.

Maintaining an Active Capability

The third area of activity during the first quarter of this 6-month assessment period involved the work to maintain an active capability and apply the VISTA system toward several target user applications. Activities in this area have included:

- improved and hardened the current operating environment
- maintained an operating system
- completed the prototype ADE and drafted the ADE users manual for VISTA
- interfaced with ARM (Global Climate Change) and made use of their knowledge base
- investigated the potential of using VISTA for portions of the Arid Site Demo.

The net finding of the entire project was that even though substantial technical progress had been made on the VISTA system, additional development efforts should largely be supported by scientific and technical users of the system. LDRD funding for this project was discontinued in February 1992.
Weapons-Grade Plutonium Denaturing

D. F. Newman (Reactor Technology Center)

This project will develop and test a methodology for neutronic design and analysis of fuels for light water reactors (LWRs) and liquid metal reactors (LMRs) to denature weapons-grade plutonium more rapidly and effectively than could be accomplished using conventional UO$_2$-PuO$_2$ mixed oxide (MOX) fuels. Preliminary studies will also be conducted on the viability of candidate materials and fabricability of the fuel system. The products will be specific recommendations for resonance absorbers and burnable absorbers to provide appropriate self-limiting and fissile depletion reactivity behavior for LWR and LMR fuels, and a general method for prediction of neutronic characteristics of fuels.

An evaluated nuclear data file suitable for use by the WIMS-E neutronic analysis computer code was prepared. The file was developed by processing available ENDF/B files for resonance absorbers and burnable absorbers that are candidate materials for tailoring the neutronic characteristics of plutonium fuels to be compatible with technical safety specifications for existing LWRs and LMRs. A letter report was issued that assesses the material properties and fabricability of candidate plutonium fuel constituents to address their technical feasibility. Preliminary neutronic analyses of LMR fuels was reported in a letter report with comparison to conventional MOX fuels in FFTF. A letter report to DOE-RL was prepared on FFTF capabilities for denaturing weapons-grade plutonium.
2.0 Center-Level Projects
2.1 Applied Physics
Application of Holographic Principles to Eddy Current Coil Impedance Data to Enhance Defect Image Resolution

J. M. Prince (Automation and Measurement Sciences)

In existing eddy current (EC) imaging techniques, the resolution is limited by the physical dimensions of the coil, which generates an unfocused image. Holography is utilized to focus the electromagnetic wave phenomena occurring in a coil/flaw interaction. This project evaluated the theoretical and experimental limits of this image resolution enhancement technique.

Experiments reveal that depth information can be resolved by using the unprocessed phase of the probe impedance, which is proportional to depth over the entire depth range of the EC test data, which is typically less than 1/2 wavelength.

It is anticipated that a three-dimensional imaging algorithm is possible by integrating the backward wave propagation algorithm for lateral resolution with a propagator function, based on the probe impedance phase, for depth resolution. Such a hybrid algorithm would provide the first accurate three-dimensional EC imaging capability in NDE. It is estimated that development could be completed in 1 year.

The holographic principle of backward wave propagation has been applied to phase-multiplied EC probe complex impedance data to produce focused images of subsurface defects. Significant improvements in the lateral image resolution have been observed. However, the wavelength/geometry dimensional relationship in EC testing does not allow satisfactory depth resolution with backward wave propagation.
Applications of Real-Time Statistical Quality Assessment

D. K. Blough (Analytical Sciences)

The primary goal of this research project is the extension of the quality assessment model developed for the Atmospheric Radiation Measurement (ARM) Program. Specifically, the statistical model was extended to handle matrix-valued time series. Robustness of the model with respect to specification of initial state variances and prior probabilities were investigated, and a demonstration software package showing some of the model capabilities was created.

The result of this work will be an enlarged methodology for real-time quality control of a variety of instruments. Extension of the model beyond the requirements of the ARM program was accomplished by developing a model capable of handling matrix-valued time series. A clearer understanding of the effects of the initial model inputs on model performance were obtained from the sensitivity analysis. Finally, a demonstration package of the model was produced to exhibit its potential to prospective customers.

Matrix-Valued Time Series

The dynamic linear model is a Bayesian methodology useful for the statistical modeling of time series. It can accommodate univariate and vector-valued time series (see for example, West and Harrison 1989). The first part of this project was to determine how these techniques could be extended to handle matrix-valued time series. After an extensive review of the literature, the work of Quintana (1987) was found to have addressed this issue and provided an affirmative answer. Moreover, Quintana goes on to discuss the multiprocess dynamic linear model for matrix-valued time series. The multiprocess form of the model has been found to be particularly well suited to the real-time assessment of data quality. In fact, such models are currently being implemented as part of the ARM program as part of its quality control procedures. One problem with matrix-valued time series is that there are two observation covariance matrices to account for; a left covariance matrix essentially for the correlation structure of the rows of the observation matrix, and a right covariance matrix describing the correlation structure among the columns of the observation matrix. The right covariance matrix can be estimated from the data in a manner analogous to that for vector-valued series. The left covariance matrix needs to be parameterized in terms of one or more "nuisance" parameters. These quantities are called nuisance parameters because while their presence is essential for model specification, they are often not of primary interest. By using the Bayesian approach developed by Gordon and Smith (1989), these nuisance parameters (and hence the left covariance matrix) can be accommodated. These is some cost in using this approach in as much as it can be demanding in terms of computation time.

By combining these results, (the multiprocess model, the results of Quintana, and those of Gordon and Smith), the laboratory now has available the capability to handle data in virtually any format. The key component of this work is that the combination of these techniques results in the maximal extraction of information from data for the purposes of quality assessment. That is, by adopting a multivariate approach to the modeling of time series, the correlation structure among observations is utilized.

Sensitivity Analysis

Univariate time series were simulated. These series contained sudden changes, the nature of which was determined by the investigator. A systematic study of the effects of tuning parameter variation on model performance was conducted. It was found that the initial settings of observation noise and the probabilities of sudden change had the greatest effects. Specifically, small initial values for both sets of parameters resulted in the model tracking the series very closely, indicating change as an all or nothing phenomenon. By increasing observation noise, fewer false positive signals were obtained.

Model performance was robust with respect to the settings of the other tuning parameters: initial distribution of the state matrix, variance inflation factors (to account for sudden changes), and sharpness of the initial distribution of the right covariance matrix.
Demonstration Software

Using the digital signal process software known as DADiSP on the SparcStation, a demonstration of the univariate dynamic linear model was developed. It simulates the real-time processing of data; as each observation is read, all relevant model outputs are updated and displayed. This includes the probabilities of sudden change: outlier, change in the level of the series, or change in the local slope. These quantities are most relevant for assessing the quality of data. A smoothed version of the data is produced along with uncertainty bounds. The local slope of the series is displayed along with uncertainty bounds (useful for detecting gradual drift in a series).

Capabilities

The result of this work is that the Laboratory now possesses the capability to monitor in real-time virtually any data gathering process. This monitoring can be used in a number of different ways:

- forecasting and prediction of sudden change is possible.
- categorizing data sets or instruments by the time series features extracted by the dynamic linear model.

Other possible applications of this methodology include:

- monitoring tank levels at Hanford (an on-line measure of the local slope of the level time series might provide predictive information on the next "burp")
- monitoring the spectra of remote sensing radars (a matrix-valued time series--rows = height in the atmosphere, columns = wave number in the spectrum)
- monitoring sudden changes in satellite data for NST (looking for electromagnetic bursts could be automated by the use of the dynamic linear model).

References


Automatic Test Generation

D. E. Buska (Computational Sciences)

This project developed prototype tools to aid in the automatic generation of test data for C programs. The developed tools did not exist previously and studies have shown that their existence would save substantial amounts of time and money in software development.

The major accomplishment was to complete a prototype which generates a C test program from a C "include" file containing typedefs and prototypes. The C files generated include routines to print and read the data structures contained in the specified include file.

The final work included testing and repair of bugs, a noontime seminar presenting an overview of our prototype tool, and writing a paper on the tool and its application.
Computational Modeling of Room Air Convection and Ventilation Effectiveness

T. J. Marseille (Analytical Sciences)

The primary objective of this research was to demonstrate how a Computational Fluid Dynamics (CFD) tool could be used to facilitate the design of a room air distribution system by predicting localized ventilation effectiveness and thermal comfort. The study also intended to highlight the difficulties in fully utilizing CFD codes for these applications.

A TEMPEST model of a single-office space forced air system was created and calculations performed to predict room air and thermal distribution for a limited set of supply air diffuser orientations/locations and airflow rates. Calculated parameters from the TEMPEST runs were used in a model to estimate thermal comfort of occupants at various locations in the office space. A pollutant source term along the floor was also introduced during each calculation, and the resulting concentrations predicted by the TEMPEST mass transport model was used to estimate local ventilation effectiveness.

Other Accomplishments

A paper on this work was submitted to the American Society of Heating, Refrigeration, and Air Conditioning Engineer (ASHRAE) for inclusion in their 1993 annual meeting conference proceedings.
Energy End-Use Data Analysis Environment and Toolkit

R. G. Pratt (Energy Sciences)

The objective of this project is to create an integrated energy end-use data analysis environment and toolkit. Such an environment would facilitate the detailed analysis and appropriate use of existing and future energy end-use data sets.

The environment would be designed to operate within the context of a distributed computing system as exemplified by our current group of networked Sun SparcStations. It would be designed to interface with and complement the new data pipeline currently under development. The analysis environment would maintain current capabilities developed on the ELCAP/REMP microVAX-based system, which has been deactivated by Bonneville, and incorporate many enhancements and additions supporting analysis and data management that have come to light through experience using that system.

The scope of the proposed tasks included the design and initial implementation of the structure of the environment, while supporting the communication necessary to ensure compatibility between the proposed analysis environment and the "data pipeline" design effort being undertaken by PNL's Energy Sciences and Computational Sciences Departments.

The initial effort on the project was to hold a series of meetings with staff involved in ELCAP/REMP and Energy Edge, the largest ESD data collection/processing/management projects. The impetus for these meetings was to integrate the activities of this research with plans to update and streamline the data processing and management software for these projects, each of which involves large end-use metered data sets. Also, there were several long-outstanding requests for access to data and information far upstream of the normal end-use data routinely delivered for analysis. Further, and perhaps more important, were the clear parallels between controlling and managing the flow of data through analysis processes and data management processes.

The view expressed by the investigators, based on their experience analyzing these large, complex time-series data sets, can be summarized by the following statement of overriding philosophy: data processing is analysis made routine. Blurring the distinction between data processing and analysis provides a very different perspective on how data processing systems, termed data pipelines here, should be constructed.

Finally, the labor and computational efficiency provided by data pipelines needs to be developed to make these capabilities more modular, adaptable, extendable, and distributable across computational platforms. The data processing steps embedded in existing PNL data pipelines are designed to be very efficient for the data from specific projects by being hard-coded into custom software, but hence are relatively inflexible in what types and intervals of data they expect, what those data represent and how they are manipulated, and the types and order of the processes that they are put through. For example, if a new or improved data quality check is developed by an analyst, it must be programmed at considerable expense and inserted into the data pipeline, or else the analyst must manually run the procedure periodically on all the data. Another example is the disaggregation of mixed heating/cooling channels into their respective components. A much more desirable environment is one where the new analytic procedure can be inserted directly into the data pipeline in its native form, without reprogramming.

Similarly, existing pipelines are not readily adaptable to the requirements of different types of data, such as that from short-term metering projects common to our DOD projects, which may involve combining sensors in new and different ways (the product of flow rates and temperature to compute heat flows in pipes or ducts, for example). Thus, a key aspect of this framework is that trying to develop the "ultimate" data pipeline (emphasis on the singular) is neither possible nor desirable, but instead attention should be focused on creating a modular toolkit from which pipelines (plural) can be constructed to meet the needs of specific projects.

These discussions fundamentally changed the scope of this LDRD effort from an analysis toolkit to an integrated data processing/analysis environment. The
excitement generated by this perspective on data processing as analysis, and the consequent shape and form suggested for the data pipeline, motivated this redirection. It was decided to focus the effort on defining a framework for evolution of data pipeline software by defining key elements and capabilities of such a system. We felt that establishing this framework was crucial, because the opportunity to completely design and construct such a system in one step appears remote. Therefore, it is essential to take advantage of existing smaller development efforts undertaken by existing and future projects by communicating this vision and defining its key elements.

In addition to laying out the requirements and schematic design of such a system, several specific concepts were developed that are central to it. These included

- defining all data into one of four classes of data types
- data pools
- processing modules
- environment/system functions
- both the concept and alpha version of a generalized storage format for data and analysis results that is compressed binary and machine independent (both using public domain software elements), and randomly accessible and updatable (key features required for efficient processing of large data sets).

Acknowledgment

PNL staff members Bill Sandusky (ESD), Dave Hostetler, Jan Schwab, and Mike Devaney (CSD) all provided valuable contributions to the vision presented here, and their contributions are hereby acknowledged.
Ensemble Averaging of Multiphase Flow Equations

L. M. Liljegren (Analytical Sciences)

The objective of this effort was to develop a multiphase flow model which describes motions at small time and spatial scales. Small-scale motions are an essential feature of turbulent flows; consequently, the ability to describe the small-scale motions is an essential feature required of a flexible multiphase flow model.

The scope of this work is to apply Delhaye and Achard's (1978) ensemble averaging equations to the mass and momentum transport equations which govern the motion of each individual phase at a microscopic level. Ensemble average equations were obtained. The method developed for the mean transport was applied to obtain turbulent kinetic energy and dissipation equations, such as those contained in turbulent flow models like TEMPEST.

This work will provide a multiphase flow model which is suitable for application to turbulent particulate flows, such as slurries. These types of models are required to ensure that the changes made to transform single-phase flow models, such as TEMPEST, into two-phase flow models are rigorously based.

Reference

Other Accomplishments
A paper based on the analysis is being prepared and will be submitted to the International Journal of Multiphase Flow.

Ensemble averaged mass and momentum equations for a particulate-fluid mixture were obtained. These formed a "two-fluid" type model. When combined to create a mixture model, this set of equations reproduced the "Einstein" viscosity correction for a mixture. This is the first two-fluid model to achieve this result.
Geographic Visualization and Animation

S. Tzemos and D. J. Bates (Computational Sciences and Analytical Sciences)

This project provided guidance on, and prototype implementation of, the use of computer-generated visualization and animation techniques, especially as applied to time-varying phenomena over geographical regions. Examples of applications were user-controlled visualization and animation of temporal data derived from supported data bases or generated for various types of models for environmental contamination plumes. These types of displays were useful in allowing researchers to quickly grasp additional details of the phenomena they were trying to understand or model and also served as excellent information tools by presenting highly technical models in an easily understandable media.

We have used animation to visualize geographically related data that vary with time. The basic Spatio/Temporal model used stores the changes between time slices in a sequence of overlays (change slices). An overlay containing the changes is defined each time there is a change. To recreate the map at a specific point in time, one starts with the base map and overlays all the change slices until the time of interest. This change slice model, although intuitively simple, integrates time into the spatial model by identifying and storing the spatial changes as they occur in time. We applied this model for a sequence of 20 quarterly change slices of ground-water tritium concentrations from the Hanford site.

The tritium data is collected at different time intervals and frequencies by several different monitoring organizations (mostly PNL site-wide, WHC Operational, and WHC Regulatory programs) and is therefore very irregular, both in time and space. Because of the animation technique chosen for the prototype (discrete time-varying planar view of a single contour level) it is necessary to produce interpolations of the data both over the same and space. For reasons of simplicity, we have decided to do time interpolation in one pass of the data and then to do spatial interpolation of the resulting data. The first step was to use the raw data to produce sets of interpolated quarterly results, each of which would be used to provide a single contour realization for input to the visualization program. The creation of the quarterly results was accomplished by the input of the raw data for each well sampled to a time series interpolation program (PROC EXPAND from the Statistical Analysis System [SAS]). These quarterly time series interpolations were then input into TIN module of the ARC/INFO GIS system to create the Triangulated Irregular Network (TIN) surface representation of the data over space. The bi-variate quintic interpolation algorithm of ARC/INFO was used for the spatial interpolation of a single concentration contour (> 200,000 pCi/L). The contour changes between successive quarters were recorded as change slices. The areas where each contour expanded were identified as positive changes while the areas from where the contour retracted were identified as negative changes. By identifying the positive changes with a different color (red) than the negative changes (the background black), we were able to depict the movement of the tritium concentration contour (tritium plume) through time.
Infrared Fiber Optic Hydrocarbon Vapor Sensor for DOE Environmental Applications

J. W. Griffin (Automation and Measurement Sciences)

The primary goal of this project was to design, fabricate, and demonstrate an infrared fiber optic sensor system for the detection and quantification of hydrocarbons (gasoline constituents) for automotive applications. The sensor system incorporated a helium-neon laser source operating at 3.39 microns and a zirconium fluoride fiber optic waveguide to sense infrared absorption in hydrocarbons due to carbon-hydrogen stretching vibrations in the range of 3.3 to 3.6 microns.

Technical progress included the following during FY 1992:

- Design, fabrication, and demonstration of an infrared fiber optic chemical sensor system suitable for monitoring hydrocarbon emissions during combustion processes.

- Incorporation of a second optical channel at 1.15 microns to allow compensation for fiber bending losses. A second channel was installed and demonstrated in the laboratory. Source for the 1.15-micron channel was secondary emission from the 3.39-micron helium-neon laser. The 1.15-micron channel was shown to be insensitive to the presence of hydrocarbons and hence, via a ratio method, it can be used to compensate for fiber movement during chemical measurements.

- Initiation of a MathCad model of the infrared fiber optic chemical sensor system to enable estimation of lower chemical detection limits, maximum allowed fiber optic umbilical length, and laser source power requirements.
Low Thrust Trajectory Optimization

N. E. Noffsinger (Energy Sciences)

The objective of this project was to develop a recognized expertise within the DOE for the solution of low-thrust, near-optimal trajectory problems. The near-term need for reliable, reproducible trade study data and mission analysis software was addressed and the groundwork for optimal trajectory determination was developed.

A major accomplishment was the analytical conditioning of the equations of motion which, when converted to a computer algorithm, obviated the need for med-trajectory coordinate transformations. This saved computing time and greatly reduced the complexity of the trajectory program. It would appear that this analytical conditioning approach could be generalized to the many-body problem and is suggested for future investigation.

A computer program was written based on the fully conditioned equation to empirically explore low-thrust trajectories earth-to-moon graze. An example was developed which shows that a near-moon graze of an OTV can be obtained without transfer between earth-centered and moon-centered coordinate systems. It is the author's understanding that with other forms of the governing equation, numerical "blow-ups" can occur when the OTV is within the SOI of the moon (Enright). What has yet to be explored is the numerical stability of this form of the equation. Hopefully, this approach will streamline numerical integration of the large number equations usually resulting from trajectory optimization efforts.

The program as written was successfully used for Earth-Moon and Moon-Earth transfer under manual control, low-thrust conditions. The next phase of effort would be to use state-of-the-are nonlinear programming techniques for automated low-thrust control. This effort will result in a much "larger" program of great utility of mission analysis and trade studies for low-thrust vehicles.

This project ended in FY 1992.
Microtechnology for Energy Applications


Microtechnology has the potential to dramatically change the way energy is consumed. Individual components are being developed, including motors, sensors, and heat exchangers. This project is focused on developing the capability to design, analyze, fabricate, and test prototype microscale systems, and sensor packages assembled from microscale components.

FY 1992 activities primarily involved the completion of reviews of the state of the art in Micro-Electro-Mechanical Systems (MEMS), including types of components currently in development, their operating features, and the microfabrication techniques used in constructing them; and Heat Transfer and Fluid Mechanics calculational methods at the microscale.

The major conclusions from the reviews include the following:

• In general, single-phase single-component fluid dynamics and heat transfer at the microscale (50-micron wide flow channels) is not significantly different from that encountered in traditional compact heat exchangers. Analytical methods and computer models are available to predict pressure drop and heat transfer for single-phase single-component applications but similar information appears to be lacking for multiphase multi-component flow.

• Extensive research has been conducted on single-phase heat exchangers and these components can be modeled, designed, and fabricated with confidence. No information was available on multiphase flow heat exchangers.

Technology Demonstration

Based on the results of the literature review, the microtechnology project team identified several candidates for the technology "proof-of-concept" demonstration. The demonstration would consist of designing, fabricating, and testing a micro-channel multiphase, multicomponent heat exchanger. The demonstration would include fabrication of micropumps for moving fluids through the exchanger.

Presentation

Pen-Based Energy Building Software

C. C. Conner (Energy Sciences)

A prototype pen-based residential energy audit methodology will be developed as a test of the feasibility of using a pen-based computer for field-based energy applications. An attempt will be made to combine voice and pen input on the prototype software.

The goal is to test the feasibility of using pen-based software in energy applications, evaluate the ability to link pen and voice software technologies, identify other pen-related technologies which need to be investigated, and produce a prototype demonstrating pen-computer feasibility in an energy application.

A residential energy audit prototype was implemented. The prototype application implements the Standard Heat Loss Methodology (SHLM) audit as used in BPA's Weatherwise Program. The software runs on the GridPad pen computer, which is carried by the auditor to the residence requiring the energy audit. The application allow the input of all required for the SHLM analysis. The results of the analysis can be stored as homeowner and utility reports, which can be viewed or printed by the auditor. The auditor can also store, retrieve, and modify audit data. The audit application includes a sketch screen which allows the auditor to create and save sketches and dimensions of the residence.

The audit software allows the input of a subset of the program's data by using voice commands. The audit application successfully demonstrated the feasibility of the integration of pen and voice.

The prototype demonstrated the feasibility and applicability of the pen-computer platform for energy application. Success with this prototype indicates the pen computer may increase the efficiency of field staff significantly.

Several applications have been identified. A new prototype will implement pen-based software for enforcement of an energy code. This will be developed in FY 1993.
Semantic Data Modeling for Scientific Data Exchange

D. E. Smith (Computational Sciences)

This project investigated the use of a reduced set of semantic data model constructs for a scientific, nuclear-engineering based application. The emphasis of the model is on component-subcomponent type aggregation. The project was limited to development of and initial testing of the reduced model using the information structure needed to capture data from a nuclear engineering computer code and transfer the results to a series of other computer codes for subsequent analyses. The project included development of the reduced semantic data model, a high-level data model for the nuclear engineering analysis domain, and data transformation routines for transferring data between the applications and the data model.

The reduced semantic data model was developed. It included hierarchical data structures to represent the "IS-A" and "PART-OF" relationships found in engineering structures. The model also included class and instance concepts, though without the method inheritance found in object-oriented programming languages. Little benefit would be realized from method inheritance in this problem domain.

The information structure developed for the nuclear engineering computer codes was the middle portion of a larger structure for representing nuclear reactors. This demonstrated that the model could be rapidly prototyped and later extended with little penalty. The structure was implemented in Quintus Prolog on a DOS platform. An extended menu structure was developed to demonstrate the functions of the data storage and exchange process. The menu structure was filled in at the bottom level for a limited subset of functions. The functions were chosen to demonstrate a deductive database approach to data generated by intentional rules.

The model will not be developed further in this project. A different implementation language would be needed to integrate the prototype into the existing network environment and to handle the volume of data expected. A full, working version would require either an extended relational database model or a deductive database model to support a production database with size, speed, and security requirements. The reduced semantic data model concepts from this project are being incorporated into the Bonneville Power Administration Common Data Model project.

Presentation

Sonar Impulse Target Strength Holography

H. D. Collins (Automation and Measurement Sciences)

The overall objective of this project was to develop a new near-field target strength technique. Sonar impulse near-field target strength holography is a new concept originating at PNL that will provide the ability to measure target signatures over a broad range of frequencies, using impulse illumination. Typically, the signatures are obtained at every single frequency, resulting in large expenditures of time and money. Also, they must be performed in the far-field, which adds additional costs and range complexities. Low frequency signatures are extremely important in the detection of targets at great distances.

A new concept, impulse target strength holography (i.e., multi-frequency) has been initiated. This concept extends the previous sonar target strength holography technique which implies single frequency imaging.

Research this year consisted of computer prediction of model two-dimensional and three-dimensional target strength with and without synthetic applied sonar absorbing material.

Holographic images were computed at an equivalent sonar frequency component (450 kHz) using the above procedure. The large target is composed of a multitude of point reflectors, and each one contributes to form the composite hologram.

The images were reconstructed in the computer by simply back propagating each of these plane waves back to the target forming the image.

Amplitude reduction analysis performed in this study indicated that the absorbing material reduced the amplitude profile approximately 40 dB.

With a single data set using the impulse technique, all target strength profiles for each discrete frequency in the pulse bandwidth can be generated in software! If we assume 1024 discrete frequencies, then 1024 target strength profiles can be generated for every aspect angle in the vertical! In other words, if the transducer beam width is ±30°, we can generate approximately 61,440 (2-D) target strength profiles.

The results of sonar absorbing material and resultant reduction in target strength values were analyzed. The peak values around 0° were reduced approximately 10 dB across an example angle profile.

The target’s three-dimensional target strength image is constructed in the same manner as the two-dimensional target strength by computing its "two-dimensional" plane wave angular spectrum, and that of a calibration sphere, and then computing the final target strength values for display. Typically a 1024 x 512 sampled hologram is capable of generating for each frequency component in the pulse 524,288 target strength values at unique far-field angles. Thus, an N x M hologram is able to generate N x M target strength values for three-dimensional display. Mathematically, we are simulating the propagation of the target’s plane wave spectrum at each frequency to the far-field receiver.

Three-Dimensional Target Strength Calculation

Target strength is computed for each angle within the transducer’s angular spectrum to generate the three-dimensional image using the following equation:

$$\sigma_{3D}(\theta, \phi) = 10 \log \frac{\left(\frac{A_x(\theta, \phi)}{A_x(\theta, \phi)}\right)^2}{A_x(\theta, \phi)} (db)$$

where

$$A_x(\theta, \phi) = \text{plane wave amplitude of the target at angles } \theta_i \text{ and } \phi_i$$

$$A_x(\theta, \phi) = \text{plane wave amplitude of the sphere at angles } \theta_i \text{ and } \phi_i$$

$$\theta_i = \sin^{-1}\left(\frac{i \lambda}{n L_z}\right)$$

2.1.15  Laboratory Directed Research and Development - FY 1992
\[ \phi_y = \sin^{-1}\left( \frac{j \lambda}{n \Delta y} \right) \]

\( n = 2 \) for monostatic (source-receiver scanning)

\( n = 1 \) for stationary source scanned receiver

(bistatic, etc.)

for

\[ i = \frac{M}{2} \pm \frac{M}{2} + 1, ..., \frac{M}{2} - 1 \]

and

\[ j = \frac{N}{2} \pm \frac{N}{2} + 1, ..., \frac{N}{2} - 1 \]

\[ L_x = N \Delta x = \text{aperture in x direction} \]

\[ \Delta_y = \text{sample distance in y direction} \]

(i.e., usually \( \frac{\lambda}{2} \))

\[ \alpha_s = \frac{r_s^2}{4} = \text{the sphere's intensity ratio} \]

The three-dimensional plots generated by the system illustrate graphically the deductibility of the target at all aspect angles. This display could be implemented to allow optimum positioning to avoid sonar detection, etc.

Source and Receiver
Statistical Measures of Aging

B. P. Hildebrand (Automation and Measurement Sciences)

This project evaluated the statistical properties of ultrasonic images of unflawed materials to determine if they could be used to predict material properties. Specially prepared stainless steel samples were scanned to provide two-dimensional images of a set of interior planes. Statistical analysis of these images were performed and characterized.

A set of five samples of stainless steel plate, previously heat-treated at 700°C for 0, 1, 18, 25, and 150 hours, was scanned with 10 and 20 MHz ultrasonic beams. The backscattered grain "noise" was digitized and recorded at a set of 128 x 128 positions over a 0.4 x 0.4-inch area. A specific time interval within the digitized A-scans was selected and analyzed for peak amplitude, which was then recorded. These recorded amplitude values were then subjected to a variety of statistical tests to determine whether a trend could be established.

It was found that several statistics exhibited a weak trend as a function of length of heat treatment. These were

- Mean, which decreased with length of heat treatment.
- Coefficient of variation, which increased with length of heat treatment.
- Standard deviation, which increased with length of heat treatment.
- Kurtosis, which decreased with length of heat treatment.
- An artificial statistic that is essentially the slope of the cumulative distribution curve, which increased with the length of heat treatment.
- Entropy, which decreased with heat treatment.

Reference

2.2 Earth and Environmental Sciences
Advanced Wind Speed Sensor

S. D. Tomich (Atmospheric Sciences)

This project investigated the use of high gauss cobalt magnets as a potential magnetic bearing for use in wind speed sensors. Due to the high cost of cobalt magnets, a set of neodymium 35 ring and rod magnets were procured. From these ring and rod sets, a mechanical fixture was constructed for testing the concept.

A second task on this project was the construction and testing of an electronic circuit, which could provide increased resolution from pulsed output wind speed sensors for use with the magnetic bearing concept. This task would prove that higher resolution data are obtainable from pulse output sensors, either the magnetic bearing sensor or other commercial pulse output devices.

A magnetic bearing set, consisting of a double-ended shaft, end magnet stops, and supporting ring magnets, was ordered and received. These parts provided the basis for construction of a simple demonstration assembly on which the application of magnet bearing support for wind speed sensing could be tested. As a totally passive system, the assembly lacked the desired mechanical stability. An active element, an electrically driven coil, was used to enhance the performance of the ring and rod assembly.

While some desired characteristics were demonstrated, the system continued to lack the stability and strength to perform well in wind speed sensing applications. Subsequent investigation into improving this assembly revealed that an active control loop would be required to yield the desired result. The active control loop would require a position sensor, electronic control, an actively driven coil, and custom miniaturization of the circuitry and assembly. Since the goal was to investigate the magnetic bearing concept as a low-cost, maintenance-free sensor, the investigation was halted due to daunting complexity presented by all of the required additional components. The early conclusion of the magnet bearing effort, and guidance from management allowed the remaining funds to be released for use on other LDRD activities within the laboratory complex.

In parallel to the magnetic bearing development, a pulse-width conversion circuit was designed and built for testing. While awaiting the procurement of the neodymium 35 components, this circuit was tested with a commercial pulse-type wind speed sensor. Data obtained from this circuit led to further investigation by the Wind Turbulence Characterization program into its use for enhancing high-speed data collection. Performance tests were run with comparisons of a low-cost cup sensor using the pulse-width conversion circuit and a higher cost DC (continuous output) wind speed sensor. The results showed that the new electronic circuit could extract the same information from a low-cost sensor that the higher cost DC wind speed sensor produced.

Since the electronic circuit that was developed for processing the magnetic bearing sensor signal showed such promise, the Wind Turbulence Characterization program began a rigorous testing and evaluation task. Coupled with that task was the integration of filtering techniques on the pulsed signal in addition to testing the electronic circuit. The results of the tests revealed that the low-cost pulse output sensor could replace the higher cost DC sensor in wind turbulence characterization research if a Gaussian filter is applied to its output signal.

Publication and Presentation


This paper describes the investigation and results of the efforts to use low-cost sensors in the turbulence characterization environment. It also clearly demonstrates that the Gaussian filter technique is a viable means of implementing low-cost sensors to obtain the necessary high speed data.
Developing a Framework for an Advanced Air Toxics Model

L. A. Mahoney (Atmospheric Sciences)

This project selected existing atmospheric dispersion modeling codes and incorporated them into an integrated software system. The result was a framework that allowed users to choose different combinations of parts of the existing models to simulate a wide variety of toxic release conditions and meteorological data sets. This advanced air toxics model (AATM) should be more widely usable than any single existing dispersion model because of its many possible combinations of modeling techniques and user-friendly interface.

The prototype (ISS) developed during FY 1992 provides a detailed, professionally presented working demonstration of the advanced air toxics model (AATM) function. The model selection module allows a user to select one of eight air dispersion models by answering a variety of questions about the problem to be solved: the nature of the emissions, the meteorological conditions, the terrain features, etc. This module provides help screens, transcript, and a partial explanation of why particular models have been selected. The AATM also contains a complete input generation module for a simple dispersion model (MPADD), and an incomplete module of a complicated model, ISCST2. The input generation routine provides the user with a graphical interface for entering data, including units conversion, help screens, default values, transcript, error prevention for complex inputs, and ready-made libraries of chemical and other important properties of emissions.
Extraction of Organic Contaminants by Supercritical Fluid Extraction

E. A. Crecelius (Marine Sciences Laboratory)

Supercritical fluid extraction (SFE) methods were developed and tested for a variety of sample matrices (sediment and tissues) and several classes of organic chemicals (polynuclear aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], and pesticides). These SFE methods were tested on certified reference materials and compared with results from conventional U.S. Environmental Protection Agency solvent extraction techniques.

Considerable research was performed to determine the current status of SFE. We attended a nationally sponsored meeting on SFE and one of our technicians attended a short course on the use and application of the technique for environmental samples sponsored by Dionex. In addition, we analyzed a number of sediment samples, including two certified reference materials (NIST 1939 and 1941) by SFE for PAHs by GC/MS and for PCB Aroclors by GC/ECD. A Dionex SRE-703 system was used. Three extraction schemes were used: CO₂ only, modified with methanol, and modified with methylene chloride. The following conclusions were made:

- Poor recoveries of PAHs and PCBs were obtained by SFE under the conditions used. Low recoveries, however, may have been caused by poor flow characteristics or collection efficiency. This seemed to be due to operator error due to the difficulty of using this system.
- Reproducibility of the SFE was generally good.
- Methylene chloride appears to be a better modifier than methanol.
- Extracts appear acceptable for direct PAH analysis by GC/MS, with no additional cleanup; however, analysis for chlorinated compounds using GC/ECD will require additional cleanup steps.
Feasibility of Using Analog Processing for Geographically Integrating Hanford Environmental Information for Technical and Nontechnical Uses

G. E. Wukelic (Geosciences)

The goal of this project was to develop, demonstrate, and evaluate a customized capability for applying advanced digital-analog processing techniques for organizing and using combinations of remotely sensed and conventional Hanford environmental data.

During FY 1991, emphasis was placed on acquiring and geographically registering Hanford imagery, maps, and ancillary information required for concept demonstration. In addition, customized software was developed to manipulate Hanford data that was required for feasibility assessment.

FY 1992 activities resulted in the enhancement of both the data base and system functionality. Extensive efforts involved interactions between PNL, WHC, and Richland Field Office (DOE-RL) personnel to solicit their interests and views relative to the analog-digital capability. Concept demonstrations and coordination activities were quite successful in confirming the value of the concept. Accordingly, a Technical Task Plan, drafted in concert with WHC personnel focusing on Hanford remote sensing and environmental data integration, is being coordinated with DOE-EM and DOE-RL personnel.

This project has provided extensive insights to Hanford environmental activities, and has enhanced coordination between PNL and WHC in the area of remote sensing and environmental cleanup. These activities have contributed to both ongoing programmatic involvements and new initiatives under consideration at the headquarters level.
Modeling of In Situ Biorestoration of Organic Compounds in Groundwater Using High Performance Computers

K. R. Roberson (Geosciences)

The objective of this project was to enhance the state of the art in biorestoration modeling using massively parallel computer architecture. Our access to experimental studies (SERF), modeling expertise (PNL, Rice) and high performance computing experience (Delta consortium, PNL, NSF Center for Research in Parallel Computing) puts us in a unique position to exploit a window of opportunity and obtain this goal.

This project consisted of porting a three-dimensional biorestoration code (as described in the background section) to a multi-instruction/multi-data (MMD) high performance computer architecture (specifically the Intel i860 hypercube and Delta computers). A technique called domain decomposition was used to parcel regions of the model to individual processors. This strategy has been verified to work and achieved linear speed up on the flow calculation component of the simulator. Simulations of a prototype biorestoration scenario with complex, heterogeneous material properties were used to demonstrate a new capability to predict results of practical field tests in a reasonable length of time.

During FY 1992, we made progress on analyzing the biokinetic models of importance to simulating dense non-aqueous phase liquid (DNAPL) degradation and formulating parallel solution methods (using the Delta machine). This progress is consistent with our stated approach and goals.

We examined the dynamics of microbial systems described by non-linear reactions. Recently, the importance of the dynamics of non-linear systems has been more fully appreciated; note in particular the general development of chaos theory. Because the mathematical description of microbial growth may contain multiple coupled non-linear equations, it may be possible to observe periodic (oscillating) or chaotic behavior in these systems (indeed, periodic behavior in some microbial systems has been observed in the laboratory). The mathematical treatment of these types of systems requires special care. This may be particularly important in the simulation and even practical application of bioremediation technologies. The ability to simulate periodic or chaotic behavior may be important to properly designing a remediation technology. We will continue to explore these systems next year to determine if periodic or chaotic behavior can be induced to increase bioremediation efficiency or further our understanding of complex process dynamics.

We have made progress on parallelizing our current approach to bioremediation simulation. We are concentrating on domain-decomposition techniques and on using the Delta (528 processors) computer. The method we use for the pressure solution is completely parallelizable and the only issue is how many iterations it takes to converge. Naturally, this is of great practical importance so we have spent our computer budget investigating this issue and also another technique—additive Schwarz. For the transport equation, there are two issues confronting parallelization; the characteristic tracking, and solving for diffusion. For incorporating diffusion, we are looking at using the explicit/implicit techniques. In these methods, we use non-overlapping subdomains and predict information on subdomain interfaces from the current solution (i.e., explicitly). We use this information as boundary conditions for implicit subdomain solutions. For problems where this method is applicable, it results in linear speed-up, proportional to the number of subdomains. We are still working to formulate the method for time-dependent problems with matrix coefficients, such as the dispersion tensor in contaminant transport. Thus, we are investigating using the explicit/implicit method as a preconditioner for the fully implicit mixed finite element method. For parallelizing the characteristic traceback, we believe we are going to rely on data decomposition. That is, let each processor track those elements which reside on that processor. The only problem is when characteristics cross several subdomains, which will probably happen rarely.
Quantum Geochemistry: Oxide Mineral Interfaces

C. J. Hostetler (U. Sciences)

The objective of this proposal was to investigate relationships between molecular-scale interactions and the macroscopic properties of selected oxide surfaces. The proposed work involves an examination of the number and types of adsorption sites near oxides surfaces at the molecular level for comparison with the same information inferred from laboratory adsorption studies and thermodynamic modeling.

A molecular dynamics model for gaseous and liquid water incorporating polarization and dissociation has been developed. This is a fundamental advance, greatly expanding the types of molecular dynamics calculations possible in aqueous systems, especially at surfaces.

The model uses an extended Lagrangian method to incorporate oxygen polarization. To obtain convergence of water cluster normal modes, the fictitious mass parameter associated with the dipole degrees of freedom must be chosen to be approximately 0.01 proton masses, although dipole masses may be set to 0.1 proton masses without changing vibrational frequencies by more than 10%. The kinetic energy associated with non-adiabatic dipolar dynamics has a strong effect on the transport behavior predicted by the model. Simulations having dipole temperatures in equilibrium with nuclear temperatures give self-diffusion coefficients which are an order of magnitude to small. The problem has been circumvented using an individual damping scheme in which all dipole velocities are set to zero whenever they have negative dot products with their associated forces. To counteract this dissipation, the nuclear degrees of freedom are coupled to either proportional or integral thermostats, each giving equivalent results for static and dynamic properties. Parameters for the model have been re-evaluated through fitting to the geometry and binding energy of the water dimer, giving improved agreement with experimental bulk water structures. The average dipole moment of the solvated water molecule in 2.3 Debye, in approximate agreement with the expected value of 2.5 Debye. Additionally, the energetic relations for gas phase ion clusters are in reasonable agreement with experiment: the proton affinity of the H$_2$O molecule is 165 kcal/mol, and the binding energy of 1, 2, and 3 H$_2$O molecules to the hydronium ion are 30, 25, and 23 kcal/mol, respectively. Simulations indicate that proton transfer involves short-lived (<1 picosecond) fivefold coordinations of hydroxyl ions.

Publication


Presentation

2.3 Life Sciences
Appliance Use and Cancer

R. H. Lovely (Epidemiology and Biometry)

The objective of this project is to test for statistically significant associations between ELF-related cancers (e.g., leukemia) and reported use of select appliances where this information exists in completed epidemiological data bases.

This project was a continuation and extension of a project conducted during FY 1991 that established "proof-of-principle" that human factors influence exposure to extremely low frequency (ELF) magnetic fields.

The New York Power Lines Project (R. G. Stevens, Principal Investigator) was identified as a study that produced a data set on appliance use by leukemia cases and random-digit-dialed case controls. Among the many appliances inquired about were three hand-held appliances that generate substantial magnetic fields and are relatively invariant with regard to source-term behavior. These were electric razors, hand-held hair dryers, and massage units. The survey questions allowed us to extract information on whether these appliances were ever used, as well as duration of use/day.

Dr. Stevens made this data set available as an ASCII file. The data set was reformatted via two statistical software packages (SPSS and SAS) with the help of BSRC. Initially, we assessed ownership and usage via univariate analysis (chi square and t-test). Massage units were owned by significantly more cases than controls and razors were used significantly more minutes/day by cases than controls. Usage of all three appliances pooled as "personal" appliances revealed significantly more use by cases than controls. No such trends were found in a random selection of four common household appliances that did not require low variance source-term behavior (e.g., dishwashers).

Subsequent to the initial analyses, the data were evaluated by stepwise logistic regression factoring in two known effect modifiers (allergies and cigarette smoking). Razor usage remained statistically associated with the disease leukemia. When the data were dichotomized at 2.5 minutes of usage/day, we obtained an adjusted odds ratio of 2.15 (1.04, 4.45, 95% IC). The observed association was for males only. No association was observed for the other two appliances, in part because there were not many observations on use of these two appliances.

Presentation

- These findings were presented at the annual DOE Contractor's review held this November in San Diego.
Development of a Ribbon Channel Plate for DNA Sequencing

R. J. Douthart (Life Sciences Center)

The overall objective of this research is to develop new technology for DNA sequencing and fingerprinting. This specific research involves development of a new gel electrophoresis technology that is a hybrid between gel-filled capillaries and ultra-thin gels. The new technology involves fabrication of a thin channelled plate. The plate consists of individual micro-channels approaching capillary dimensions, etched or machined into it. Each channel is isolated from its neighbors by a thin wall and, therefore, acts as an individual gel micro-ribbon. The plate, however, can be filled with gel at one time guaranteeing consistency in the micro-ribbons, with respect to composition and casting variables.

A gel assembly unit holds the plate casting and has built into it a thermostated baffle that allows very rapid heat exchange. The advantages of rapid heat loss with concurrent partial decoupling of running temperature and electroositive heating associated with gel-filled capillaries, and the ease of preparation and consistency of slab casting are incorporated in the ribbon channel plate.

Using a small prototype casting device and channel plate, the following results were obtained:

- Using dyes, electrophoretic viability was demonstrated for channels of various sizes. Supersaturated dye solutions were used. It was very difficult to avoid overloading even when using the smallest available Hamilton syringe.

- Experiments with sequence ladders indicated separation into distinct bands. A constant problem encountered was streaking due to leakage into the space between the sealing gasket and the covering glass plate. This can be alleviated to some extent by prior sealing of the gasket to the cover plate with a thin film of glycerol. Loading from a vertical position into a tiny well causes much of this problem as the gasket tends to be torn away by the loading syringe.

- Preliminary experiments with the small test plate attached to the drum device gave indication that bands could be satisfactorily deposited on the nylon membrane at least four times faster than normal electrophoresis. However, a host of experimental difficulties were encountered and no usable sequence information was obtained. Most of the difficulties were traceable to the vertical positioning of the plate assembly with respect to the drum. Near the end of the fiscal year a horizontal assembly was designed and built, however, there was no time left to test it.

![Ribbon Channel Plate](image-url)
Development of Direct Skin Beta Dosimeter

T. E. Hui (Health Physics)

Portable skin dosimeters are needed for personnel who are continually exposed to beta radiation. Most of the common detectors are passive and do not allow for a direct continuous measurement of radiation doses. Development of a direct skin beta dosimeter, to which this project is directed, overrides this problem. In addition, the detector should be reasonable in cost and reliable.

In this pilot test of the feasibility of the beta skin dosimeter, two solid state planar radiation detectors were placed in two legs of a Wheatstone bridge. This imbalance would be proportional to the skin dose. This approach is a new idea in which the output from the detector is the current instead of the pulse heights. This enables one to measure the skin dose directly.

We managed to detect a small signal due to the beta radiation. However, the contribution to the signal due to the variation of temperature is much greater than that due to the beta radiation alone. This led to poor signal-to-noise ratio and poor statistics in the detector output. Since the goal of this project is to design a rugged detector capable of measuring skin dose in actual field situations, temperature dependence is a great concern. We feel that without a significant investment and a major change in design, even though we got positive signals from beta radiation, this idea is not practical to be adopted for widespread use.
Exposure Biomarkers for Reproductive and Developmental Toxicity

L. E. Sever (Epidemiology and Biometry)

This project is focused on developing approaches for applying exposure biomarkers in reproductive and developmental toxicity risk assessment.

This project included review of the literature and ongoing research, discussions with laboratory scientists, establishment of collaborative relationships, writing of a paper for the peer-reviewed literature, and development of concepts for follow-on proposals.

Literature was obtained and reviewed regarding biomarkers and reproductive and developmental toxicity risk assessment. A computerized bibliographic retrieval system has been established, as has access to an online reproductive toxicity database REPROTOX.

Concepts for possible projects were explored with researchers from several academic institutions. Expanded opportunities for the use of biomarkers in studies of reproductive hazards are likely to develop in the next few years.

Publication

Feasibility Study of the Reduction of Background Using Proportional Counter in Coincidence

D. R. Sisk (Health Physics)

This project was directed toward determining the feasibility of reducing background by using proportional counters in coincidence. The study was limited to evaluating the capability of the technique to reduce background levels and increase survey scan speeds in beta detection.

The data indicated that there are two competing effects when operating two counters in coincidence: measurement geometry and coincidence circuitry. The effect of measurement geometry causes a reduction in sensitivity. Two counters operated in coincidence have a lower background count rate than a single counter. A reduction in sensitivity must be accompanied by a reduction in the square of the background count rate if the detection limit of two counters in coincidence is to at least equal that of a single counter.

The sensitivity of a single counter exceeded that of two counters in coincidence by a factor ranging from 1.7 to 3.0 depending on the maximum beta particle energy. The factor decreased with increasing maximum beta particle energy. Measurements indicated that the background count rate of two counters in coincidence was less than that of a single detector by a factor ranging from 4.0 to 2.9. The factor decreased with increased ambient gamma exposure rate. The results indicate that the detection limit of the two counters in coincidence ranged from 15% lower to 76% higher than the detection limit of the single counter.

A significant improvement in the detection limit of an instrument using two proportional counters in coincidence compared to a single proportional counter was not realized. The proportional counters used in the study should be redesigned to minimize the density and atomic number of the walls and windows. This would further reduce the background count rate by decreasing the probability of gamma ray interactions. In addition, the two counters should be combined so that only one window separates the counters. This would improve the measurement geometry. Studies should also be performed with a plastic scintillator replacing one or both counters.
Modeling of Images of the Human Body for Applications in Absorbed Dose Calculations

G. Akabani (Health Physics)

A new differential volume phantom was designed to study the possibilities of generating new and more accurate information concerning dose volume distributions and radionuclide distribution in the human body (dynamic processes are included).

This new phantom was based on physiological, anatomical, and metabolic variables obtained from an individual patient. The variables generated a specific phantom that will simulate only that specific patient. Data required were obtained from MRI studies and could be easily used to reconstruct images for use as geometrical input. The use of current methods for generating tri-dimensional organ surfaces was studied for use in this research. Biophysical dynamic models of the human body were included. The models allowed simulations of the movement of radioactive material within organs and systems and led to more accurate estimates of radioactive material deposition.

A phantom was used to generate a three-dimensional file containing information related to regions and organs of the human body. The mathematical representation of the phantom was transformed into a geometrical array of voxels containing information of the different regions and organs of the body. This representation was used as an input for the Monte Carlo code, electron gamma shower (EGS4) to calculate energy deposition patterns. By using a Monte Carlo, it was possible to sample the radionuclide distribution for a specific organ or tissue in the human body. Preliminary results were obtained by using the computerized phantom in which the kidneys were considered as a source organ containing a uniform distribution of Tc-99m. Energy deposition patterns were recorded for the whole trunk of the phantom. As a result, it was possible to obtain dose volume histograms for different organs and regions of the computerized phantom. After successfully generating energy deposition patterns in specific regions and tissues of the body, a similar step was undertaken using MRI images of the human body.

The development of dosimetric models that address current issues of bone research have been of primary interest. Software and hardware were developed to assess the structure of bone based on image techniques that greatly extend the understanding of the relationship between absorbed doses to specific bone tissues and biological effects. Images of the bone provided the basic site-specific information of the morphology, cell populations, and radionuclide distributions. Dosimetric models were developed for bone marrow, trabecular bone, and Haversian canals based on Monte Carlo transport of electrons, photons, and alpha particles, and a detection system was designed for the imaging of radionuclide distribution in bone samples. Radionuclide distributions will be calculated for bone tissues and, along with dosimetric models, will be used to assess a cause-effect relationship with the respective biological outcome.

Publication

Non-Ionizing Radiation (NIR) Hazard Assessment Software

M. H. Smith (Health Physics)

The objective of this project was to develop a software package that will help a user perform NIR hazard analysis computations for radiofrequency and microwave emitters. Programming work was done to create an integrated software package that performed NIR hazard analysis based on the IEEE/ANSI radiofrequency radiation protection guide. The Numerical Electromagnetic Reflector Antenna (NEC-REF) code was installed and run on PNL VAX and HP9000 computers. This code, written by Ohio State University, models the power density at selected points in space from radiofrequency and microwave emitters. A separate computer software package was developed by PNL to interface with the NEC-REF code. The PNL code allows for easy entry of data and compares NEC-REF output against the values in the IEEE/ANSI radiofrequency protection guide. This comparison feature allows a user to perform a detailed hazard assessment of a radiofrequency/microwave emitter.

The PNL code written as an interface for the NEC-REF code was also developed as a stand-alone software package called RFP. The RFP software can be used to quickly calculate estimates of emitter hazards. This software can be run on any IBM-PC compatible computer. PNL personnel used this software in the field during FY 1992 to estimate microwave emitter hazards before performing field measurements.
The goal of this project was to develop and improve our capability to identify and quantify cells proliferating in target tissues of rodents as a result of exposure to radiation or toxic chemicals, and utilize this information to study the relations between cell proliferation and cancer induced by physical or chemical insults.

During FY 1992, we developed the capability to utilize a monoclonal antibody assay for an endogenous protein, proliferating cell nuclear antigen (PCNA) as an indicator of cell proliferation in tissues of laboratory rats. PCNA is a nuclear protein expressed in late G1 and S phases of proliferating cells. The PCNA assay enables us to retrospectively examine cell proliferation rates of target tissues from studies in which animal numbers are not sufficient for cell proliferation studies using exogenous labels such as tritiated thymidine or BRDU.

Our work during FY 1992 was concentrated on the development and refinement of the use of the PCNA assay for quantifying cell proliferation in nasal epithelium of rats. The nasal mucosa is a frequent target tissue for inhaled xenobiotics, and is particularly difficult to assay using immunohistochemical techniques because it requires decalcification, a process which masks antigenic sites, prior to processing for histology.

We compared cell proliferation rates in the nasal mucosa of rats exposed to glutaraldehyde using the PCNA assay with data generated on this project in 1991 using the BRDU assay. All three labeling methods (BRDU pulse, BRDU pump, and PCNA) demonstrated increased cell proliferation in glutaraldehyde-instilled rats, compared with saline controls. These data correlated well with data from microscopic examination of H&E sections indicating increased hyperplasia in groups of rats instilled in the pulse studies compared with the pump studies. Good correlation was also present in individual rats in both studies between numbers of nuclei labeled with BRDU or PCNA and hyperplasia present in H&E-stained sections.

Presentation

We presented the results of these studies at the International Symposium of Societies of Toxicologic Pathologists in Nagoya, Japan, in April 1992, and at the annual meeting of the Society of Toxicologic Pathologists in Phoenix, Arizona, in June 1992. We have a manuscript in preparation on this work.
2.4 Materials and Chemical Sciences
Analytical Atomic Spectroscopy Using Ion Trapping Techniques

D. W. Koppenaal (Materials and Chemical Sciences)

This project was directed at the development of ion trapping techniques, using both electrodynamic (Paul-type) and magnetic (Penning-type) ion traps, for use in advanced chemical characterization and analysis endeavors involving trace elements and radionuclides in the environment. We conducted a series of spectroscopic experiments using ion traps as atomic reservoirs (test tubes) to enable enhanced detection and characterization of atomic or organometallic species. Investigation was performed of ion traps for isotopic ratio determinations, as well as elemental/radionuclide measurements.

Experiments with a modified commercial ion trap mass spectrometer (ITMS) were performed to assess the capability of ITMS for isotope ratio measurements and quantitation, with particular emphasis toward development of a new generation of inorganic and isotopic analysis methods. Investigations focused on developing design strategy for ion traps specifically tailored for such work (as opposed to current commercial ion traps designed for organic MS analyses). A design incorporating a larger trap volume, higher radio frequency (RF) drive frequency, and lower RF voltage will bring specific improvements in space charge and dynamic range effects, higher tolerance to field imperfections, higher resolution, and lower power requirements for an elemental/isotopic ion trap. Funding is currently being sought for construction and evaluation of this tailored trap design. ITMS experiments using Xe and Kr gases indicate that isotope ratio precisions of 10 to 12% RSD are immediately attainable with conventional instrumentation. Complete elimination of persistent oxide and other polyatomic ions has also been demonstrated, providing purely atomic ion peaks for ratio measurements. The ability of ITMS to selectively isolate and detect analyte peaks in the presence of ubiquitous matrix ion concomitants was also demonstrated. Finally, conceptual plans for in-trap laser desorption/laser ablation of single environmental indicator particulates were developed for future proposal submission.

Presentation

Catalyst Design

M. A. Lilga (Chemical Sciences)

The objective of this research was to probe structure/activity relationships in bimetallic catalysts in order to better understand how metal centers in close proximity can work together to carry out useful organic transformations. This work was built on previously gained knowledge and focused on dimeric hydrogenation catalysts. The results of this research program will be of value in designing catalysts that have desirable properties, such as specificity.

A ligand-bridged dimeric chromium complex, 1, was prepared and characterized by IR, UV/Vis, and NMR spectroscopies. Mass spectral data are also being collected. Crystals suitable for an x-ray crystal structure determination have been obtained and are now being analyzed.

The hydrogenation of 1,3-butadiene was found to be about twice as fast for the unbridged analog, 2, compared to the bridged analog 1. Upon consumption of the 1,3-butadiene, the final distribution of butene isomers is approximately the same for both 1 and 2, with trans-2-butene being the major product. Butane is not produced in significant quantities. The identical product distribution for the two catalysts was unexpected based upon literature results in which no 1-olefin was found in pentadiene hydrogenation.

Either the extra methyl group present in the pentadiene exerts a sufficient steric or electronic effect to influence the product distribution or the higher \( H_2 \) pressure used in the literature method affects the catalysis.

Isomerization of cis-2-butene occurred to give mostly trans-2-butene and some 1-butene; both catalysts gave about the same distributions after nearly 2 days for the bridged and 4 hours for the unbridged catalysts. A similar experiment with 1-butene and the bridged catalyst produced a substantial amount of cis-2-butene. This result is interesting because the cis isomer is the thermodynamically less stable isomer and suggests an active role by the catalyst in the isomerization. These results also differ from those reported in the literature in which migrations of double bonds in the presence of 2 did not occur. Initial results of 1-butene isomerization by 2 were very different from those with 1; little or no isomerization was observed. Duplicate experiments are needed to verify these results.
Laser-Induced Fluorescence in Multicomponent Refractory Oxide Hosts

N. J. Hess (Materials Sciences)

Increased interest in the fields of phase stability, phase transformation mechanisms, and kinetics have led to development of new experimental techniques that allow access to sustained, simultaneous high pressure and temperature conditions. However, the lack of pressure and temperature sensors that are reliable under these extreme experimental conditions have limited continued advancement. The objective of this research was to explore the fundamental mechanisms of fluorescence properties of rare-earth doped multicomponent oxides, and use this information to design new materials with optimized properties which could be used as in situ, optical pressure and temperature sensors.

During FY 1991, the glycine-nitrate powder (GNP) synthesis technique was used to investigate the compositional stability of $Y_3Al_5O_{12}$ powders and thin films with the garnet structure (YAG) and to determine the kinetics of the YAG crystallization process. Using samarium-doped YAG (Sm:YAG) powder samples, the effects of dopant concentration and chromium contamination on the Sm fluorescence intensity, lineshape, and lifetime were determined. In addition, measurements of the pressure dependence of Sm:YAG fluorescence lifetime on single crystal samples have indicated that the lifetime is pressure-insensitive. The temperature dependence of the fluorescence lifetime and frequency shift of Sm:YAG and Cr:Al$_2$O$_3$ (ruby) thin films, synthesized from GNP precursor solutions, were utilized in an ongoing DOE-BES program as interfacial strain and temperature sensors for the determination of stress-temperature history of laser damage phenomena in amorphous optical coatings.

During FY 1992, fluorescence spectroscopy, XRD, and NMR were used to investigate the thermal phase stability, transformation kinetics, and solid solution of Sm-doped Y$_2$O$_3$-Al$_2$O$_3$ oxides generated by GNP. These oxides, considered as potential hosts for sensor development, included structural modifications of YAlO$_3$, Y$_2$Al$_4$O$_9$, and Y$_3$Al$_5$O$_{12}$. The results of this study indicate that both starting materials and processing technique strongly influence the phase stability and crystallization kinetics of these oxides and that fluorescence spectroscopy can be used successfully to probe the kinetics of the structural transformations of materials.

Fluorescence spectroscopy, in conjunction with Raman spectroscopy and XRD, were used to determine the phase of Sm:YAG and Sm:ZrO$_2$ powders and thin films synthesized using a modification of the GNP technique. In place of glycine as the fuel, varying mixtures of urea and carbohydrazone were combined to generate crystalline high temperature phases directly, without resorting to sintering that is required if glycine is used. In general, the resulting powder consists of highly crystalline, 100 μm particles. Atomic Force Microscopy revealed that thin films produced from the urea-carbohydrazone precursor solutions are of higher optical quality than those generated by glycine-based solutions.

Continued collaboration with Dr. David Schiferl, LANL, has resulted in the extension of the frequency shift of laser-induced fluorescence of Sm:YAG to higher pressures and temperatures. The results of this collaborative effort has generated sustained interest by the mineral physics and geophysical communities. High pressure, single-crystal x-ray diffraction experiments conducted by Dr. Schiferl indicate that YAG lattice compresses isotropically. This result suggests that a theoretical examination of the pressure dependence of fluorescence frequency shift is a solvable problem. New collaborative interactions were initiated with Professor Alexandra Navrotsky, Princeton University, on the determination of thermochemistry of refractory oxides; with Dr. Charles Prewitt, Carnegie Institute-Geophysical Laboratory, on the synthesis of hexagonal "perovskites"; and with Dr. Kurt Sickafus, LANL, on neutron irradiation effects on Sm:YAG fluorescence and its pressure dependence.
Publications


D. Schiferi, W. D. Bennett, and N. J. Hess "High Pressure, Single Crystal, X-ray Diffraction of Sm:YAG to 5 GPa" (in preparation).
Material Structural Properties and Physics of Scintillators

M. Bliss, P. Reeder, and R. A. Craig
(Nuclear Chemistry, ONST, and Automation and Measurement Sciences)

The goal of this project was to examine the relationships between material structure, electronic relaxation processes, and light output in scintillating materials by developing a microscopic understanding of the electronic relaxation process in scintillating materials and how structural and chemical factors affect them.

The scintillation light output of a series of silicate glasses has been determined for a fixed electron energy deposition. The glasses are cerium-doped, alkali-silicates. Scintillation light output measurements were made as a function of alkali, alumina, ceria concentration, and of annealing history. In this system, the cerium outer electron cloud serves as a sensitive probe of the local glass structure. From these measurements, a sensitivity matrix relating the light output to the structure was developed. A conceptual model for the behavior of the light output has been developed in which nonbridging oxygens serve as the primary trap for ionizations. The light output also appears to be related to the equilibrium phases that would be expected to crystallize from the various glass compositions. A composition series for which sodium was substituted for lithium indicates that the relationship between matrix structure and energy transfer to the rare earth ion is more complex than originally expected. Light output varied significantly in these series even though the concentration of nonbridging oxygens was held constant.

Other Accomplishments

- Dr. Marvin Weber of Lawrence Livermore Laboratory presented data from this study at Crystal 2000 (a major conference on scintillating materials).
- An article for submission to Nuclear Instruments and Methods is in preparation.
Photoacoustic Laser Calorimetry for the Determination of Rate Constants

J. A. Franz and S. T. Autrey (Chemical Sciences Department)

The objective of this project was to develop methods, instrumentation, and software for measurement of rates of reaction by the method of photoacoustic laser calorimetry. The capability to measure both heats of reaction and to measure rate constants for simultaneous or sequential reactions is a method of broad potential application to solution of biological and chemical problems.

This project began in FY 1991. A complete photoacoustic detection system was constructed, including a new short path detection cell. During FY 1992, the system was applied to the determination of quantum yields for free radical formation in the photolysis of disulfides, and to obtain kinetic and static photoacoustic spectra (as opposed to calorimetry). This work provided important supporting data which demonstrated that phenyl disulfide, when photolyzed in organic solvents, leads to PhS· radical pairs which undergo rapid intersystem crossing on the ca. 10-picosecond time scale from the triplet to the singlet manifolds.

In FY 1992, the system was modified by adding a lock-in amplifier module. This allowed us to obtain photoacoustic uv-visible spectroscopy of low concentrations of substrates. Finally, computer programs to deconvolute two or more simultaneous photoacoustic waves was obtained, which can be used to obtain more accurate thermochemical determinations of bond strengths and heats of reaction. The work supported under this project has allowed us to complete instrumentation with important applications in soil science and organic free radical chemistry.

The instrumentation is now being used to measure heats of formation of novel organic and organometallic free radicals, RSS· and Bu₃SnS·, and organic substrates in reactions with soil minerals. These are examples of systems for which quantitative thermochemical data is very difficult to obtain. Results from follow-on studies are being collected for publication in related studies of sulfur and tin-centered free radicals. This LDRD project has provided an important capability for the study of interactions of organic substrates with soil minerals, of importance to environmental restoration.

Publication

A publication describing this work is in preparation in collaboration with Prof. Gary Schuster, Department of Chemistry, University of Illinois at Champaign-Urbana for submission to J. Phys. Chem.
2.5 National Security Technology
Evaluation of Foreign Satellite Radar Data

K. L. Steinmaus (Geosciences)

Conducting an early examination of the quality of Almaz imagery in the first commercially available satellite radar data base was the emphasis of the LDRD activity. If the spatial resolution (15 meters) and the dynamic range (gray levels) are as advertised, this commercially available imagery could have important monitoring implications for DOE's national security activities.

During FY 1991, Almaz imagery was requested for two study areas: Puget Sound, in western Washington, and the Yakima Training Center (YTC), in eastern Washington. Due to a combination of acquisition complications and poor image quality, progress in the evaluation was slow and in some cases, inconclusive.

The evaluation of the YTC imagery could not be conducted as planned because the image received did not cover the requested area for comparative analysis with optical imagery. The vendor refused to provide a na-cost replacement image. Upon analysis, the data that was received did have the 15-meter spatial resolution claimed by the vendor. However, image quality (based on dynamic range) was 3-bit (8 gray levels) as compared to the technical specification of 5-bits. Results comparing image quality of Almaz to U.S. Geological Survey radar data were developed.

Puget Sound imagery was acquired to evaluate oceanographic implications of the Almaz radar data. Difficulties were encountered in acquiring high resolution bathymetry data corresponding to the radar data acquired. Commercial sources of bathymetry data proved inadequate in this evaluation. Naval personnel at Bangor Submarine Base were contacted and arranged for the transfer of a digital bathymetry data base to PNL. Based on the analysis conducted, it appears that subsurface topographic features are characterized in the data by wave patterns at the surface.
EVALUATION OF FOREIGN SATELLITE RADAR DATA

May 1991 Almaz Image of Puget Sound Showing Olympic Mountains on Left and Bangor Naval Base in Right Center

Subset of Puget Sound Image Showing Bangor Naval Base. (Note: Triangular Radar Returns in Center of Image.)

Side-Scan Sonar Data of Puget Sound Verifying Existence of Subsurface Triangular Feature
Lithium Isotopes in Particles

J. F. Wacker (Chemical Sciences)

The feasibility of using PIMS (Particle-Inlet Mass Spectrometry) for measuring lithium isotopes in particles from various particulate samples was examined in this LDRD activity. The proposed work on lithium complements earlier work that demonstrated the capability of PIMS to measure uranium isotopes in single particles from various types of environmental samples (airborne dust, soils, etc.). Reports are available describing PIMS for uranium isotope measurements (including operation of the instrument).

The main issues in establishing the feasibility of using the PIMS technique for lithium isotope ratio measurements are background, sensitivity, and precision of measuring isotope ratios on rapidly varying ion signals. The first two issues depend on the oven temperature while the third depends on using multi-isotope detection.

Measurements of mass spectral backgrounds were made by scanning the background before and after analyzing samples. In general, mass spectra showed the presence of peaks at $^6$Li and $^7$Li and a mass independent background in between these isotopes with a count rate 2 to 3 orders of magnitude smaller than that of the $^7$Li peak. Typical backgrounds for $^7$Li from a new oven run at 2400°C were in the 100 counts/s range, whereas signal levels were 10,000 counts/s after samples had been run.

Optimum oven temperature was determined by briefly admitting small amounts of particulates into the PIMS instrument and observing the decay time for the resultant lithium signals. An oven temperature between 1800 and 2000°C results in a 0.1 to 1-s ion burst signal that rapidly decays to the background level. However, the background signal slowly rises from 100 to 10,000 counts/s as material is continuously admitted into the PIMS instrument. Baking the oven for 15 min or more reduced background levels to 100 to 1000 counts/s.

Measurements of samples with known amounts of lithium were used to determine the sensitivity of the PIMS instrument. An order of magnitude estimate of the sensitivity was made using a sample of NBS 2704 (river sediment), which contains ~ 50 ppm of lithium (this concentration is not certified by National Institute of Standards and Technology). With a 1-mg sample, detection limits for $^6$Li are estimated as 1 ppb natural lithium. In an individual particle, $<10^7$ $^6$Li atoms should be detectable.

Lithium Isotope Ratios

Lithium isotope ratios were measured on both the lithium background from the oven and on a 2-mg sample of NBS 2704 loaded into a cold oven (which produces a constant signal as opposed to the burst signal produced by admitting the particulate material while the oven is hot). Signal levels decayed with time constants ranging from 1 hour to a few minutes, depending on the oven temperature. Since the PIMS instrument was not configured for simultaneous measurement of lithium isotopes, isotopic measurements were made by scanning the mass spectrum (the instrument also lacks peak-jumping capabilities as this was not required for developing PIMS for measuring uranium isotopes). Scanning the mass spectrum in the lithium mass range (5 to 8 amu) required several minutes, which, combined with the decaying signals, resulted in low precision in the measured isotope ratio. However, the average lithium isotope ratio was 12.8 for many measurements, using both the instrument background and NBS 2704 samples. These values are consistent with the natural ratio of 12.3 given the uncertainties in the time dependence of the lithium signals and the read-time correction for the ion detector.

This project demonstrated that lithium isotopes could be measured and that the backgrounds due to lithium dispersed throughout the sample did not mask the signals produced by particles with high lithium concentrations. Follow-on work should include modifying the existing PIMS instrument for simultaneous measurements of both lithium isotopes.
Remote Identification Research and Development

L. W. Brackenbush (Health Physics)

The purpose of the LDRD activity was to characterize materials and matrix polymers for use in the infrared and to demonstrate the concept.

This was a new project initiated in FY 1992 to develop and characterize new phosphor materials that emit in the near infrared. Investigations prior to initiation of this project, demonstrated that it is possible to create a new class of phosphors that emit in the visible light region with conversion efficiencies as high as 10% to 20%. As a result of this work, several new phosphors were created using a proprietary process developed at PNL. These phosphors emit near infrared light with conversion efficiencies of about 1%, which is not as efficient as hoped, but still quite adequate for the uses envisioned for these new materials. The new phosphors emit from about 900 nm to 1600 nm and appear to be quite stable with time and moderate temperatures. It also appears to be possible to create unstable phosphors, i.e., phosphors that fade and lose all of their luminescent properties within a few days.

A demonstration of how these new materials could be used for remote identification was performed in the laboratory. Several potential sponsors who may be interested in these types of materials were contacted. Because of the sensitive nature of the concept and potential applications, the method of production of the phosphors will not be disclosed.
2.6 Reactor Technology
Advanced Targets

M. E. Cunningham (Reactor Systems, Fuel and Materials)

The objective of this project was to investigate opportunities and the potential for developing target materials for producing tritium using alternate advanced targets with a primary focus on particle accelerator technology.

Material on proposed target designs for production of tritium using proton accelerators was collected and reviewed (this material included information on funding and organizations that were already involved). A letter report was prepared that summarized this information. Based on this effort, it was concluded that sufficient technical capabilities currently existed within the national laboratory system to support near-term DOE program needs for advanced targets for proton accelerators. The activity was concluded at that point.

In October 1992, Brookhaven National Laboratory (BNL) contacted the Tritium Target Development Program to obtain information on fabrication of, and tritium extraction from, ceramic lithium targets. BNL is one of the principal national laboratories involved in the accelerator targets. Those contacts are continuing. This contact, while in the same subject area, was separate from the LDRD activities described above; however, information gained from the LDRD activity has been useful during the discussions with BNL.
Definition of Observables to Facilitate Transparency

T. W. Wood (Nuclear Systems and Concepts)

This project developed and tested a methodology for selection and specification of observables, which could best provide a degree of transparency for disarmament processes. The methodology was tested by application to a set of processes typically conducted at a single U.S. site. The method developed has immediate application to ongoing analyses of arms control issues and policy.

The nuclear disarmament process entails extensive activity in weapons dismantlement and materials processing and conversion. Based on current expectations, this process will be followed by utilization of weapons Pu and U in the fuel cycle. Information that confirms the extent and details of the dismantlement process is of national security value.

Even though this process may not be subject to well-defined and prearranged verification procedures, it may still be possible to gain valuable information about this process within a framework of "transparency." Such a framework has been described as the most likely environment for monitoring future arms-control agreements, and would consist of the opportunity to freely observe the inputs and outputs of the dismantlement process, without necessarily being able to observe the dismantlement or conversion activities first-hand.

This project was scoped to define observables which best facilitate such transparency and develop an analytical method which could be used to interpret them in terms of important national security questions.

This definition and methodology will facilitate transparency and make it a better substitute for specific verification arrangements.

A review of potential observables was made from defense fuel cycle descriptions, including a "matrix" of potential observables prepared this fiscal year by ONST and ongoing work within the Nuclear Archeology Project. Based on this review, this activity was focused on definition of the value of observations of weapons materials isotopic content, and providing a calculational framework within which these measurements can be interpreted. In concept, these measurements provide information relevant to two national security issues: validation of the quantity of weapons materials produced, and the confirmation that materials converted for fuel-cycle use actually originated from weapons. The same basic calculational approach could be used to investigate the material origin issue.

The quantification of the value of information from such measurements, as a function of their frequency, accuracy, and level of aggregation, could at least conceptually, be accomplished using a stochastic simulation model such as Production Complex Model (PCM). This model has been developed by NSC and used extensively in calculation of weapons materials production. An analysis of PCM capabilities showed that minor modifications were required to model these problems. These modifications were conducted under this project and provide for detailed tracking of isotopes associated with specific weapons, and materials from weapons dismantlement, within the model. The modifications were documented in memorandum form.
Eddy Current Methods/Applications Development

H. G. Powers (Reactor Systems, Fuel and Materials)

This project was directed toward achieving a better understanding and interpretation of eddy current response signals from coatings, such as aluminides, which may simultaneously exhibit changes in thickness, conductivity, and magnetic permeability. A report describing the work performed and the results achieved was prepared.

Based on the results of experiments performed, it was demonstrated that different intermetallic phases within the aluminide coating have different magnetic properties to which a proportionate change in response is revealed by a properly configured eddy current test. Measurement of phase composition in this manner is, to the author's knowledge, novel and believed to be of significant value since the functional performance of aluminide coatings in almost any application would appear to be related to phase composition, and the only methods of inspection in current commercial use are destructive.

Publication

Plot of Normalized Reactance Versus Normalized Resistance and Frequency Using Standard Probe
Plot of Normalized Reactance Versus Normalized Resistance and Frequency Using Modified Probe
International Reactor Safety

S. W. Heablerin (Nuclear Systems and Concepts Department)

Concern regarding safety of the commercial power reactors designed by the former Soviet Union (FSU) has reached new levels. This project will develop a technical approach to these issues that will allow for unique PNL capabilities to be enhanced to support DOE's role in global undertakings to upgrade the safety of FSU reactors.

The direct output of the project will be a series of reports dealing with specific issues, such as technical description of RBMK design and operations, assessment of safety enhancement needs, FSU and/or eastern European energy economic assessments, as technical safety enhancement descriptions.

White papers were developed in the area of RBMK safety and in application of U.S. expertise to the problem of conversion of the Russian military production reactors to safe non-weapons production applications. Institutional contacts have included an extensive interchange with the Moscow Institute of Nuclear Safety. In addition, agency contacts have been made with the RBMK design NIKEIT. Contacts were also made with the Massachusetts Institute of Technology, who expressed interest in joint efforts in FSU-designed reactor safety research.

The FY 1992 project supported initial efforts to develop a RELAP5 thermal hydraulics model of a single RBMK coolant channel. The initial objective of this model is to provide understanding of the pressure tube failure accident in Leningrad during spring 1992. The effort was begun late in the fiscal year, but did succeed in bringing the code to operational status on the RSA HP-750 workstation, initial collection of design information, and generation of approximately 20% of the hydraulic model description.
Tools for Reactor Analysis

A. W. Prichard (Nuclear Systems and Concepts)

The reactor analysis area offers new opportunities in analysis and design enhancements for the Soviet-designed pressurized water reactors in use within the Soviet Union and the former Eastern Block countries, and the area of nuclear materials production proliferation assessments. This project provided the preparation of reactor analysis tools that can be applied to these areas. Specific objectives included: developing a reactor lattice model of a Soviet VVER pressurized water reactor, preparing a plan for the development of a whole core model of a Soviet VVER pressurized water reactor, and completing an intelligent proliferation assessment tool demonstration.

A lattice physics model was developed for the VVER reactors. Due to the complexity of the input to the lattice physics code WIMS-E, a computer program was written to generate WIMS-E input decks. This program enables reactor analysts to perform parametric studies with minimum efforts. A series of WIMS-E and Monte Carlo (MCNP) calculations were performed for pin cell and assembly models. Preliminary results show that WIMS-E and MCNP results are not in good agreement. However, the MCNP model has a known error, correcting the error in MCNP should improve the agreement between the two codes. A plan for the development of a whole reactor core reactor model was written.
2.7 Waste Technology
CEPOD Treatment of Hazardous Organics

J. E. Surma (Waste Technology Center)

The goal of this project is to demonstrate that the Catalyzed Electrochemical Oxidation (CEO) technology can effectively destroy the hazardous organics with the required efficiency of six nines or greater. The scope of work involved small-scale tests of the technology in the BCL laboratory with PNL support. Six tests in all were completed. All required analysis was performed to fully assess the destruction efficiency of the process.

A complete electrochemical system was fabricated and tested. Results on surrogate materials indicate the process is a viable substitute to incineration for hazardous organic chemicals. This system will be transferred to Battelle Columbus Laboratory (BCL) where further testing will be completed in the surety facility.
Destruction of Organics with Corona Discharge

W. O. Heath (Waste Treatment Technology)

The primary objective of the proposed activity is to unambiguously establish the feasibility of using electrical corona to decompose organic compounds adsorbed on soil particles with and without the additional presence of adsorbed humic materials. The decomposition reaction, if successful, will effectively convert adsorbed nonvolatile compounds into volatile byproducts that can be easily removed by conventional soil-venting techniques. A second objective will be to investigate corona discharges for removing organic wastes from a gas stream, such as off-gas from the ISV process or the effluent gas from air strippers used for treating groundwaters. The most successful outcome would be to establish typical conditions and exposure-durations required to achieve complete oxidation for most organic wastes to benign compounds (like carbon dioxide and water). These objectives will be met using a versatile bench-scale corona-discharge reactor that will be developed in the first three months of this project.

Using the same bench-scale corona-discharge reactor, further experiments were performed to investigate the destruction of trichloroethylene (TCE) in air. TCE was selected because it is a common pollutant in industrial and DOE operations. For these experiments, an off-gas handling system was developed to enable TCE and moisture to be added as vapors to the ambient-pressure air stream entering the reactor. Instrumentation was added to allow the humidity, pressure, and temperature of the air entering and exiting the reactor be measured and recorded. An on-line gas chromatograph with a flame ionization detector (GC/FID) was used to measure and record TCE concentrations entering and leaving the corona reactor. This apparatus enabled TCE destruction to be determined as a function of inlet concentration and humidity, type of particles in the reactor bed, and the voltage applied to create the corona.

Several experiments were conducted to determine the best particle size, shape, and composition for the reactor bed. In general, it was found that smooth glass beads worked very well, and significantly better than sand particles or beads of Teflon or other materials. With glass beads in a fixed bed, it was found that TCE could be destroyed with a >99% destruction efficiency at TCE inlet concentrations as high as 2000 ppmv, and flowrates on the order of 2 scfm. The principal corona destruction byproduct appeared to be hydrochloric acid, indicating complete mineralization of the TCE. Total power required to produce the corona was on the order of 100 W. This corresponds to an energy cost on the order of $0.35 per pound of TCE destroyed, which is roughly 1/20th the energy required for other advanced technologies like UV oxidation. These initial results were far better than expected, demonstrated the feasibility of electrical corona for destroying organic compounds in process gases, and completed the second and final research objective.
Enhanced Bioremediation Using In Situ Heating

W. O. Heath (Waste Treatment Technology)

The objective of this activity was to determine whether electrical heating could be used to accelerate in situ bioremediation and to evaluate the suitability of six-phase electricity for this purpose. Denitrification conditions were used for this study because experimental variables (e.g., availability of the electron acceptors) are generally more controllable than for aerobic conditions, and analytical methods for measuring the metabolic reactants and products are routinely used in this laboratory. Also, because denitrifiers are facultative aerobes, demonstrating an increase in denitrifying metabolism can be a good indication that aerobic metabolism can also be increased.

Tests were performed using a sealed 40-L glass vessel fitted with a six-phase electrode array and containing groundwater-saturated silica sand inoculated with facultative anaerobes. Acetate was used as the electron donor. Five tests were performed with and without electrical heating to determine its effect on the rate of denitrification. It was found that electrical heating to an optimum metabolic range of 30° to 35°C significantly accelerated denitrification rates compared to rates under simulated aquifer conditions (11°C). This effect was found to be caused by temperature differences alone, with the presence of electric fields having no detectable effect on microbial activity. Radial temperature profiles established by six-phase heating were relatively flat, with a typical variation of ± 1°C at any given time. By contrast, soil temperatures were found to vary as much as ± 8°C in the vertical direction, with hotter temperatures near the top of the heated zone and colder temperatures at the bottom. When only the bottom of the laboratory aquifer was heated, thermally driven mixing of the simulated groundwater appeared to occur, leading to better temperature uniformity in the vertical direction (± 3°C). Further work is recommended to optimize the vertical placement of electrodes within an aquifer to achieve the best balance between temperature uniformity and thermally induced mixing to maximize rates of biodegradation while improving nutrient distribution.
In Situ Vitrified Barrier Ring

J. S. Tixier (Waste Treatment Technology)

The objective of this project was to demonstrate the ability to use ISV technology to generate a ring-shaped vitrified soil block. An engineering-scale ISV melt was conducted with the purpose of generating a vertical wall having a ring-shaped horizontal cross section; that is, similar to a traditional ISV monolith yet not melting in the middle. Following the test, the ISV monolith was excavated and its integrity examined qualitatively. The size, shape, and wall thickness of the ring was evaluated.

During FY 1991, the ISV system was modified and prepared for the test. In FY 1992, a test was conducted, which established the feasibility of the concept by initiating a ring-shaped melt. However, as the process continued, the melt progressed selectively downward on one side of the ring while the other side cooled, thus establishing a melt with a semicircular cross-section. It was discovered that the difficulty was caused by the lack of independent phase control which prevented operators from adequately directing the flow of current between the electrodes. Following an analysis of the system, the power control system was modified to increase operator control and another test was conducted. The second test also initially established a ring, but the level of control was inadequate to achieve complete balance and the process developed three separate melts between the electrode pairs. Evaluation of the process showed that, while it is possible to establish a ring-shaped melt, additional research is needed to achieve ring melt progression to produce a cylindrical melt.

Following the two ISV ring tests, conceptual design of modified equipment has been made. The components are relatively simple and a system will be constructed and tested during the FY 1993 portion of the project.
In Situ Vitrification Depth Enhancement and Subsurface Melt

L. E. Thompson (Waste Treatment Technology)

This project conducted a bench-scale ISV test and related numerical studies with the purpose of investigating methods to enhance melt depth and to evaluate methods to melt from the bottom up. This additional ISV capability, if successful, will more than double the applicable sites that can be treated by ISV by increasing the melt depth capability. Additionally, the ability to melt from the bottom up is a new idea that could result in new applications for the ISV technology including vitrified barriers or the treatment of buried energetic waste forms.

In FY 1992, analytical studies were conducted to calculate the upward heat flux that would exist in a subsurface ISV melt. Inputs from TEMPEST code outputs were used in the analyses, particularly for cases involving limited insertion depths of the electrodes into the molten pool with the presence of a void above the molten soil. The calculations indicated that a significant heat flux would exist under a variety of conditions. Subsequently, a test plan was prepared and approved and the bench-scale system prepared for the test.

A 10KW, two-electrode test was conducted by initiating a melt at a depth of 1.2 m and propagating the melt upward approximately 0.6 m during a period of approximately 30 hours. Due to subsidence, as the melt grows, a subsurface void is formed above the molten pool. To maximize the upward heat transfer, three methods were used to keep the void size to a minimum. The first method involved the use of a fill addition tube; however, this method was not fully successful. The second method involved lanceing the top dome and allowing the soil above the melt to flow into the dome. This second method worked well, but was not considered optimal for field implementation. The third method used a natural pathway adjacent to the electrodes. This third method worked well. Throughout the test, the electrodes were retracted to maintain an electrode insertion depth in the molten pool of approximately 2 to 4 cm. This results in high temperatures (> > 1700°C) in the upper portion of the melt and correspondingly supports increased heat transfer to the top of the void. As the electrodes were retracted as the melt propagated upward, the lower regions of the melt cooled and solidified as predicted by the initial calculations. Sufficient data was collected for use in subsequent studies for scale-up and model validation.

Once the melt had sufficiently cooled, it was excavated and the monolith removed for examination. During the excavation process, a saturated region of soil surrounding the monolith was observed. It is suspected that a water reflux condition was established at the 100°C isoband and likely consumed a significant percentage of the total power. Ideas were generated for field applications that could be used to minimize the potential for a reflux condition. Post-test observations of the monolith revealed that the top of the molten soil dome did not adhere to the electrodes which allowed for sufficient clearance around the electrodes to allow soil to flow into the dome.

Enhancements to electrode designs could exploit this situation by, for example, using electrodes configured with threads or drill bits. By simply rotating the electrodes, the threads would result in soil being conveyed into the void.
Waste Processing Modeling and Innovation

C. C. Chapman (Waste Treatment Technology)

The objectives of this project included the following:

- Develop a general mass and energy balance with a simplified cost model that allows a preliminary cost estimate for diverse DOE waste streams.
- Use the cost model to identify high cost elements which can be reduced through innovation and subsequent research and development.
- Complete computer models of alternate designs that can further reduce costs.
- Exploit the technology through tests, studies, and other activities to make waste vitrification more cost competitive to less environmentally sound treatment methods.

Characterization of Wastes for Vitrification

To provide sufficient information about the potential for vitrification of wastes, several fundamental characteristics are needed. Some of the important characteristics include weight fraction water, fraction organics, fraction as char, and loss on melting. A simplified procedure for obtaining these data were developed to provide a nearly consistent method. This data sheet allowed the characterizer to quantify key processing data. This data could then be used to estimate the costs for its vitrification treatment and provided estimates of volume reduction, needed chemical additions, required energy inputs, and other process related data. Real samples were characterized and data generated for the following waste materials:

- cardboard recycling waste
- de-inking sludge
- hog fuel, hog fuel fly ash, hog fuel bottom ash, and hog fuel bottom and fly ash
- plating sludge
- sewage sludge
- sewage sludge incinerator ash
- Hanford grout
- concrete
- municipal solid waste (MSW) after recycle.

Mass and Energy Balance

The objective of this work was to develop a simple mass and energy balance for the vitrification process that could generate data useful for preliminary design and costing of vitrification systems for a wide variety of waste streams. Special emphasis was placed upon combustible wastes. Important parameters include off-gas flows, supplemental energy requirements, potential gaseous pollutant concentrations, and glass production rates. This objective was accomplished by developing an Excel spreadsheet which takes a user-defined input stream and calculates simple mass and energy balances as described below.

The first section of the spreadsheet allows the user to define the waste stream composition in terms of components such as paper, plastic (either as a group or by individual type), dirt, food waste, rubber, etc. The ultimate analysis of the mix of feed components defined by the user is then calculated and passed on to the mass and energy balances. The ultimate analysis is calculated using data from the literature which has been entered in the spreadsheet. Additional waste components are easily added to the spreadsheet.

The calculated composition of the waste mixture is automatically input into the mass and energy balances. Other user inputs include the waste feed rate, percent moisture, off-gas temperature, supplemental fuel, melter power, glass former additives, and solids carryover. Using these parameters, the mass and energy balances are calculated for the following simple melter process.

The process is viewed as a black box with inputs of waste, air, glass formers, supplemental fuel, and electrical power. The outputs are molten glass and off-gas. In the black box, the waste is completely
combusted and sufficient excess air or supplemental fuel is added to bring the off-gas temperature to the specified value. The energy content of the waste is determined from general correlations from the literature. Sulfur and chloride are assumed to be completely converted to either sulfur dioxide or hydrogen chloride. Any metals in the feed are assumed to be converted to oxides, and along with the oxides in the feed, are heated to specified outlet temperature for the molten glass. Five percent of the energy contained in the waste feed is assumed to be lost to the environment.

Although this is a simple view of the vitrification process, it provides a meaningful estimate of the necessary parameters to be used in preliminary cost estimation for a wide variety of waste streams. The mass balances are also easily modified to include variations to the basic melter process described above.

Waste Treatment Cost Estimating

Using a commercial software package, a spreadsheet cost model was developed. Equipment and material costs for a plant with a fixed size were extracted from existing data. If the desired plant size differed from this reference, scaling factors were used to estimate different equipment costs. These factors were extracted from "Plant Design and Economics for Chemical Engineering" by Peters and Timmerhaus. Operating labor costs were estimated from experience at PNL and related plant operations. Off-gas equipment sizing was estimated by linking to the mass and energy balance spreadsheet described above. Waste characterization data, when available, were inserted into both the mass and energy balance spreadsheets and the cost model. These data were used to calculate the amount of consumables such as electric power, chemical additions, water, and natural gas. This permitted the end user to insert relevant plant and waste data and arrive at a representative processing cost. To account for the equipment costs, a pay-back period and interest rate could be changed. All these costs were broken out and then summed.

The development of the model provided the following general and specific benefits:

• provides a rapid and convenient method for providing cost estimates

• provides a comprehensive listing of factors that must be considered for every plant or remediation project

• exposes what is less well known and needs further refinement

• identifies the high-cost items and leads the developer to focus on these factors in developing innovations and prioritizes future research

• permits the developer to define what is cost sensitive for different waste streams, site specific conditions, and different operating parameters.

Cost estimates for a broad variation of waste streams were completed and included

• contaminated soils such as Idaho’s buried wastes, Fernald’s soils, Weldon Spring sludges, and Hanford soils

• combustible wastes such as mixed waste, TRU, and low-level waste combustible trash

• plating sludges from Warner Robins Airforce Base

• sewage sludges

• foundary sands

• municipal solid wastes

• medical wastes

• paper recycling de-inking sludges.

Terra-Vit Thermal and Electrical Modeling

Waste melters were conceived to continuously process hazardous wastes into a non-hazardous glassy product. However, many designs have proven to be extremely expensive to build. The materials of construction and labor for installation can economically affect the feasibility of constructing the system for many waste types. The Terra-Vit melter was conceived to overcome these cost issues. This melter design requires little man-made materials for construction, as it uses an earthen pit for the glass cavity. Therefore, the only required high-temperature materials are for the lid, which covers the melt area.
The thermal behavior for the Terra-Vit melter is critical for its design. The melting point of soils can be as low as 1000°C, therefore, a glass melt zone in the earthen pit with an average temperature of 1500°C could transfer heat through the surrounding soil and possibly violate the integrity of those areas providing structural support for the melter lid and process equipment. Hence, the computer modeling of the thermal behavior of the melter is key to a successful design.

Three physical drivers of the thermal behavior of the Terra-Vit system were identified as fundamental to the effective modeling of the melter. These are thermal, electrical, and convective flow (of the glass) for the entire system and surrounding soil. Although each of these drivers is integral in the true understanding of the system, the first level of modeling effort was to address the thermal and electrical drivers only.

TEMPEST, a finite element analysis program developed at PNL, was used to model the melter. The following set-up parameters were used in TEMPEST for the Terra-Vit modeling.

- Melter Lid Configuration: Circular
- Melter Lid Positioning: Grade level
- Lid Diameter: 25 feet
- Electrode Spacing: 8 feet
- Electrode Depth: 3 feet
- Cooling Wall Depth: 10 feet
- Plenum Height: 4 feet

The electrical field was run to obtain an average temperature setpoint of 1500°C within a 4 feet by 7 feet area between the melter electrodes. The soil characteristics were obtained from Hanford soil data, and the plenum space (the air space above the melt) was assumed to maintain a constant temperature of 800°C.

The analysis proved that the cooling wall configuration would indeed contain glass mobilization since isotherms no greater than 300°C appear in the cooling wall regions. Additionally, supporting areas of earth 5 feet from the cooling walls appear capable of uninhibited support integrity.

Waste Glass Castings

For waste vitrification to reach its greatest potential, it needs to exploit the nonhazardous, structural and chemical characteristics of the discharge waste glass. That is, it needs to change the discharged glass into a useful material and not be a waste.

Since a liquid glass is produced from the wastes, a broad range of products are readily achievable. However, thermal fracturing of large glass castings discourages this type of use. The objective of this activity was to determine if a concept of wire reinforcing could overcome this limitation. Using laboratory furnaces, it was demonstrated that this technique could be used to produce large blocks without cracks. Objects weighing over 6 pounds with a thickness over 2 inches were produced without careful annealing. These results are encouraging.

For wastes that cannot be used commercially such as DOE radioactive contaminated soils and materials, this technique could be used to produce large castings that can be handled conveniently with a minimum of packaging costs. For example, to package the contaminated and treated sludges at Fernald's operable unit number 1 requires over 185,000 steel boxes that cost $700 per box. The total packaging costs for this application would be about $130 million dollars. Using this wire reinforcing technique, over half of these packaging costs could be avoided. Although it has not been decided to vitrify soils at Hanford, if vitrification is used for contaminated soils or buried waste treatment, this "packaging technique" could save hundreds of millions of dollars.
Acronyms and Abbreviations
## Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AATM</td>
<td>advanced air toxics model</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AFS</td>
<td>Andrew File System</td>
</tr>
<tr>
<td>AI</td>
<td>artificial intelligence</td>
</tr>
<tr>
<td>AMOS</td>
<td>Aging Management Optimization Software</td>
</tr>
<tr>
<td>AN</td>
<td>1-aminonaphthalene</td>
</tr>
<tr>
<td>ANL</td>
<td>Argonne National Laboratory</td>
</tr>
<tr>
<td>ANP</td>
<td>aminonaphthalene</td>
</tr>
<tr>
<td>ANSI</td>
<td>American National Standards Institute</td>
</tr>
<tr>
<td>APS</td>
<td>advanced photon source</td>
</tr>
<tr>
<td>AREST</td>
<td>Analytic Repository Source-Term</td>
</tr>
<tr>
<td>ARM</td>
<td>Atmospheric Radiation Measurement</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Materials</td>
</tr>
<tr>
<td>AVS</td>
<td>Application Visualization System</td>
</tr>
<tr>
<td>BES</td>
<td>Basic Energy Sciences</td>
</tr>
<tr>
<td>BLC</td>
<td>bond-length conserving</td>
</tr>
<tr>
<td>BNL</td>
<td>Brookhaven National Laboratory</td>
</tr>
<tr>
<td>BPA</td>
<td>Bonneville Power Administration</td>
</tr>
<tr>
<td>BPDE</td>
<td>benzo[a]pyrene diol epoxide</td>
</tr>
<tr>
<td>CAR</td>
<td>classification and regression tree</td>
</tr>
<tr>
<td>CASA</td>
<td>Computer Aided Site Assessment</td>
</tr>
<tr>
<td>CFD</td>
<td>computational fluid dynamics</td>
</tr>
<tr>
<td>CHWI</td>
<td>Child Health and Welfare Index</td>
</tr>
<tr>
<td>DAP</td>
<td>Digital Acquisition Processor</td>
</tr>
<tr>
<td>DoD</td>
<td>U.S. Department of Defense</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>DOE-ER</td>
<td>U.S. Department of Energy, Energy Restoration</td>
</tr>
<tr>
<td>DOE-HEDP</td>
<td>U.S. Department of Energy, High Energy Physics Division</td>
</tr>
<tr>
<td>DOE-OHER</td>
<td>U.S. Department of Energy, Office of Health and Environmental Research</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>DSOM</td>
<td>Decision Support for Operations and Maintenance</td>
</tr>
<tr>
<td>EASI</td>
<td>Electronic Assistant for Scientific Information</td>
</tr>
<tr>
<td>EC</td>
<td>eddy current</td>
</tr>
<tr>
<td>ECMWF</td>
<td>European Center for Medium Range Weather Forecasting</td>
</tr>
<tr>
<td>EESC</td>
<td>Earth and Environmental Sciences Center</td>
</tr>
<tr>
<td>ELF</td>
<td>extremely low frequency</td>
</tr>
<tr>
<td>EM</td>
<td>Office of Environmental Restoration and Waste Management</td>
</tr>
<tr>
<td>EMF</td>
<td>electromotive force</td>
</tr>
<tr>
<td>EMSL</td>
<td>Environmental and Molecular Sciences Laboratory</td>
</tr>
<tr>
<td>ENDOR</td>
<td>electron-nuclear double resonance</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EPIC</td>
<td>erosion productivity import calculator</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>ER&amp;D</td>
<td>Exploratory Research &amp; Development</td>
</tr>
<tr>
<td>ESDIAD</td>
<td>electron stimulated desorption/ion angular distribution</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>ET</td>
<td>evapotranspiration</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>FFTF</td>
<td>Fast Flux Test Facility</td>
</tr>
<tr>
<td>fn</td>
<td>fibroactin</td>
</tr>
<tr>
<td>FSU</td>
<td>former Soviet Union</td>
</tr>
<tr>
<td>FT-ICR</td>
<td>Fourier transform ion cyclotron resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FY</td>
<td>fiscal year</td>
</tr>
<tr>
<td>GCC</td>
<td>Global Climate Change</td>
</tr>
<tr>
<td>GChM</td>
<td>Global Chemistry Model</td>
</tr>
<tr>
<td>GCM</td>
<td>Global Climate Model</td>
</tr>
<tr>
<td>GIS</td>
<td>geographic information system</td>
</tr>
<tr>
<td>GNP</td>
<td>glycine-nitrate powder</td>
</tr>
<tr>
<td>GPS</td>
<td>Global Positioning System</td>
</tr>
<tr>
<td>GUI</td>
<td>graphical user interface</td>
</tr>
<tr>
<td>HEC</td>
<td>hydroxyethyl allulose</td>
</tr>
<tr>
<td>HIT</td>
<td>homogeneous isotropic turbulence</td>
</tr>
<tr>
<td>HPCCI</td>
<td>High Performance Computational Chemistry Initiative</td>
</tr>
<tr>
<td>HPLC</td>
<td>high-performance liquid chromatography</td>
</tr>
<tr>
<td>HVAC</td>
<td>heating, ventilating, and air conditioning</td>
</tr>
<tr>
<td>HX</td>
<td>heat exchanger</td>
</tr>
<tr>
<td>IDT</td>
<td>interface development tools</td>
</tr>
<tr>
<td>IEEE</td>
<td>Institute of Electrical and Electronics Engineers</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ISV</td>
<td>in situ vitrification</td>
</tr>
<tr>
<td>ITMS</td>
<td>ion trap mass spectrometer</td>
</tr>
<tr>
<td>IV</td>
<td>intensity voltage</td>
</tr>
<tr>
<td>K_d</td>
<td>distribution factor</td>
</tr>
<tr>
<td>KPNO</td>
<td>Kitt Peak National Observatory</td>
</tr>
<tr>
<td>LDA</td>
<td>laser doppler anemometry</td>
</tr>
<tr>
<td>LDRD</td>
<td>Laboratory Directed Research and Development</td>
</tr>
<tr>
<td>LEED</td>
<td>low-energy electron-defraction</td>
</tr>
<tr>
<td>LET</td>
<td>linear energy transfer</td>
</tr>
<tr>
<td>LIMS</td>
<td>laser ionization mass spectrometry</td>
</tr>
<tr>
<td>LMR</td>
<td>liquid metal reactor</td>
</tr>
<tr>
<td>LO</td>
<td>Lowell Observatory</td>
</tr>
<tr>
<td>LOWESS</td>
<td>locally weighted regression and smoothing scatterplots</td>
</tr>
<tr>
<td>LUAM</td>
<td>Land Use and Agricultural Model</td>
</tr>
<tr>
<td>LWR</td>
<td>liquid water reactor</td>
</tr>
<tr>
<td>M&amp;CSC</td>
<td>Materials and Chemicals Science Center</td>
</tr>
<tr>
<td>MARS</td>
<td>multivariate adaptive regression spline</td>
</tr>
<tr>
<td>MBR</td>
<td>model based reasoning</td>
</tr>
<tr>
<td>MDS</td>
<td>Molecular Dynamics Simulation</td>
</tr>
<tr>
<td>MINK</td>
<td>Missouri, Iowa, Nebraska, and Kansas</td>
</tr>
<tr>
<td>MMC</td>
<td>metal matrix composite</td>
</tr>
<tr>
<td>MOX</td>
<td>mixed oxide</td>
</tr>
<tr>
<td>MRI</td>
<td>magnetic resonance imaging</td>
</tr>
<tr>
<td>mRNA</td>
<td>messenger ribonucleic acid</td>
</tr>
<tr>
<td>MSRC</td>
<td>Molecular Science Research Center</td>
</tr>
<tr>
<td>MSW</td>
<td>municipal solid waste</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Association</td>
</tr>
<tr>
<td>NDE</td>
<td>nondestructive evaluation</td>
</tr>
<tr>
<td>NEC-REF</td>
<td>numerical electromagnetic reflector antenna</td>
</tr>
<tr>
<td>NIEHS</td>
<td>National Institute for Environmental Health Sciences</td>
</tr>
<tr>
<td>NIH</td>
<td>National Institute of Health</td>
</tr>
<tr>
<td>NIOHS</td>
<td>National Institute for Occupational Safety and Health</td>
</tr>
<tr>
<td>NIR</td>
<td>non-ionizing radiation</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NSLS</td>
<td>National Synchrotron Light Source</td>
</tr>
<tr>
<td>NWS</td>
<td>National Weather Service</td>
</tr>
<tr>
<td>OHER</td>
<td>Office of Hanford Energy Research</td>
</tr>
<tr>
<td>ONST</td>
<td>Office of National Security Technology</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>OTA</td>
<td>Office of Technology Assessment</td>
</tr>
<tr>
<td>PAH</td>
<td>polynuclear aromatic hydrocarbon</td>
</tr>
<tr>
<td>PAS</td>
<td>photoacoustic spectroscopy</td>
</tr>
<tr>
<td>PCB</td>
<td>polychlorinated biphenyl</td>
</tr>
<tr>
<td>PCM</td>
<td>Production Complex Model</td>
</tr>
<tr>
<td>PCNA</td>
<td>proliferating cell nuclear antigen</td>
</tr>
<tr>
<td>PCR</td>
<td>polymerase chain reaction</td>
</tr>
<tr>
<td>PET</td>
<td>polyethylene terephthalate</td>
</tr>
<tr>
<td>pi</td>
<td>isoelectric point</td>
</tr>
<tr>
<td>PIMS</td>
<td>particle-inlet mass spectrometry</td>
</tr>
<tr>
<td>PIT</td>
<td>partial induced turbulence</td>
</tr>
<tr>
<td>PIV</td>
<td>particle image velocimetry</td>
</tr>
<tr>
<td>PML</td>
<td>polymer multilayer</td>
</tr>
<tr>
<td>PNL</td>
<td>Pacific Northwest Laboratory</td>
</tr>
<tr>
<td>PP</td>
<td>pulse programmer</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>RAAS</td>
<td>Remedial Action Assessment System</td>
</tr>
<tr>
<td>RCAR</td>
<td>Root Cause Analysis Research</td>
</tr>
<tr>
<td>RDBMS</td>
<td>Relational Database Management System</td>
</tr>
<tr>
<td>RMO</td>
<td>Rattlesnake Mountain Observatory</td>
</tr>
<tr>
<td>RPV</td>
<td>remotely piloted vehicle</td>
</tr>
<tr>
<td>RTDS</td>
<td>rapid thermal decomposition of precursors in aqueous solutions</td>
</tr>
<tr>
<td>SCG</td>
<td>single-cell gel</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SFE</td>
<td>supercritical fluid extraction</td>
</tr>
<tr>
<td>SGFET</td>
<td>suspended gate field effect transistors</td>
</tr>
<tr>
<td>SGM</td>
<td>Second Generation (Edmonds Reilly) Model</td>
</tr>
<tr>
<td>SNL</td>
<td>Sandia National Laboratory</td>
</tr>
<tr>
<td>SPF</td>
<td>superplastic forming</td>
</tr>
<tr>
<td>SRL</td>
<td>Savannah River Laboratory</td>
</tr>
<tr>
<td>SSCP</td>
<td>single-strand conformational polymorphism</td>
</tr>
<tr>
<td>SSI</td>
<td>Software System Infrastructure</td>
</tr>
<tr>
<td>TCE</td>
<td>trichloroethylene</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TIEM</td>
<td>The Integrated Earth Modeling</td>
</tr>
<tr>
<td>TIN</td>
<td>Triangulated Irregular Network</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>UIMS</td>
<td>User Interface Management Systems</td>
</tr>
<tr>
<td>USDA</td>
<td>U.S. Department of Agriculture</td>
</tr>
<tr>
<td>USETT</td>
<td>User Software Evaluation Test Tool</td>
</tr>
<tr>
<td>UST-ID</td>
<td>Underground Storage Tank Integrated Demonstration</td>
</tr>
<tr>
<td>WBS</td>
<td>work breakdown structure</td>
</tr>
<tr>
<td>XAFS</td>
<td>x-ray adsorption fine structure</td>
</tr>
<tr>
<td>XAS</td>
<td>x-ray adsorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>YTC</td>
<td>Yakima Training Center</td>
</tr>
</tbody>
</table>
END

DATE FILMED

5/28/93