Laboratory Directed Research & Development

Pacific Northwest
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ANNUAL REPORT 09

PNNL-19318

Laboratory Directed Research and Development Annual Report

Fiscal Year 2009

March 2010

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the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

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Acknowledgments

Pacific Northwest National Laboratory's LDRD Program office is grateful for the support received throughout the year, particularly while preparing this Annual Report. Special appreciation is given to the Laboratory leadership who shape PNNL's strategic initiatives and whose vision and understanding of the Nation's technological needs help guide and refine the content of PNNL's LDRD portfolio. In addition, we are especially appreciative of the many research staff who perform the research and provide their annual reports, and to the technical and administrative management of PNNL's directorates within which R&D is pursued.

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Pamela Hartsock, Technical Editor
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Stacy Schulze, IT Analyst

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Materials Science and Technology

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Nuclear Science and Engineering

Physics

Laboratory Director's Message

PNNL scientists and engineers are making important scientific discoveries and delivering valuable technical solutions critical to our Nation's future. They work across a broad range of activities with wide-ranging impact on our enduring missions of science, energy, environment, and security. Within these areas, we are distinguishing ourselves through world-leading science and technology aimed at our four institutional leadership positions:

- Design and scalable synthesis of materials and chemicals
- Climate change science and emissions management
- Efficient and secure electricity management from generation to end use
- Signature discovery and exploitation for threat detection and reduction.

Our discretionary investments, especially LDRD, are key to advancing these leadership positions and delivering on our mission outcomes. These investments help us to build our S&T capabilities and to capitalize on PNNL's talents—all while tackling current and projected problems facing our nation.

We have seen first-hand the benefits of leveraging the discoveries from these investments, which are described in this document. We carefully conduct our LDRD program in compliance with the objectives and guidelines outlined in the DOE Order. And we use rigorous internal and external peer review to maintain the scientific value and soundness of the program and the research projects it enables.

It is with great pride in our researchers' accomplishments that I present PNNL's Fiscal Year 2009 Laboratory Directed Research and Development Annual Report.

Mission Overview

As a U.S. Department of Energy (DOE) Office of Science (SC) national laboratory, Pacific Northwest National Laboratory (PNNL) has an enduring mission to bring molecular and environmental sciences and engineering strengths to bear on DOE missions and national needs.

Our vision is to be recognized worldwide and valued nationally for leadership in accelerating the discovery and deployment of solutions to challenges in energy, national security, and the environment.

To achieve our mission and vision, we provide distinctive, world-leading science and technology in:

- The design and scalable synthesis of materials and chemicals
- Climate change science and emissions management
- Efficient and secure electricity management from generation to end use
- Signature discovery and exploitation for threat detection and reduction.

PNNL leadership also extends to operating EMSL: the Environmental Molecular Sciences Laboratory, a national scientific user facility dedicated to providing integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences.

Established in 1965 with 2200 employees and facilities comprising the Hanford Site research laboratories, PNNL continued its support of Hanford Site operations, expanded its nuclear fuel cycle research, and focused on developing advanced reactor designs and materials, fabricating and testing novel reactor fuels, and monitoring and protecting human health and the environment. Since then, PNNL has evolved into a leading multidisciplinary national laboratory with a long-standing reputation for advancing scientific frontiers through world-class research and development.

PNNL is operated by Battelle Memorial Institute, a private, non-profit, science and technology enterprise that explores emerging areas of science, develops and commercializes technology, and manages laboratories. Total Laboratory funding in FY 2009 was $940.1 million. In addition to SC, principal PNNL customers include DOE's Offices of Energy Efficiency and Renewable Energy, Environmental Management, Fossil Energy, Electricity Delivery and Energy Reliability, the National Nuclear Security Administration, the U.S. Department of Homeland Security (DHS), U.S. Department of Defense (DoD), U.S. Nuclear Regulatory Commission (NRC), and the National Institutes of Health (NIH).

Laboratory at a Glance

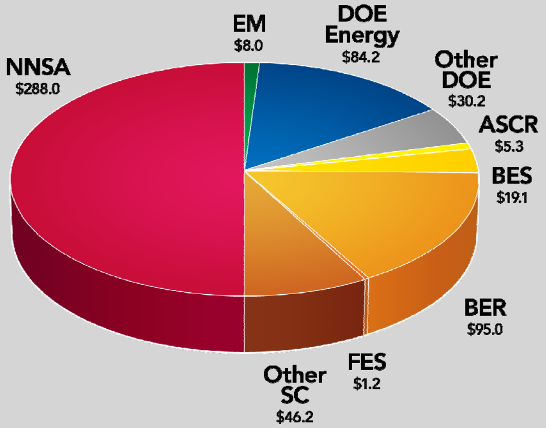
Location: Richland, Washington
Type: Multiprogram Laboratory
Contract Operator: Battelle Memorial Institute
Responsible Site Office: Pacific Northwest Site Office
Website: http://www.pnl.gov/

Physical Assets

- 350 Acres DOE, 250 Acres BMI
- 2,120,200 gsf, 709,060 gsf DOE (225,000 gsf SC, 483,897 gsf EM); 391,000 gsf BMI; 972,778 gsf Leased and Other
- Replacement Plant Value: $104M (SC Only)
- Deferred Maintenance: $38K (SC Only)
- Asset Condition Index: 100%
- Mission Critical: 1.0 (Excellent)
- Mission Dependent: 1.0 (Excellent)
- Asset Utilization Index: 1.0 (Excellent)

Human Capital

- 4150 Employees (FTEs)
- 136 Postdocs
- 375 Students
- 1941 Facility Users and Visiting Scientists



FY 2009 Lab Cost: $903.1M
FY 2009 Total DOE Funding: $577.2M
FY 2009 WFO: $141.9M
FY 2009 WFO % of Lab Operating: 16%
FY 2009 DHS Funding: $184.1M

Introduction

U.S. Department of Energy (DOE) Order 413.2B sets forth DOE's policy and guidelines for Laboratory Directed Research and Development (LDRD) at its multiprogram laboratories. DOE Order 413.2B requires that each laboratory submit an annual report about its LDRD activities to the Cognizant Secretarial Officer. This document is the Pacific Northwest National Laboratory (PNNL) LDRD annual report for fiscal year (FY) 2009.

Program Overview

A national laboratory must establish and maintain an environment in which creativity and innovation are encouraged and supported in order to fulfill its missions and remain viable in the long term. As such, multiprogram laboratories are given discretion to allocate a percentage of their operating budgets to support research and development projects that align the Laboratory's and DOE's missions and support the missions of other federal agencies, including DHS, DOD, NIH, and others.

DOE Order 413.2B establishes the Department of Energy's policy and guidelines for LDRD at its multiprogram laboratories. LDRD is "research and development work of a creative and innovative nature, which is selected by the director of a laboratory, or his/her designee, for the purpose of maintaining the scientific and technological vitality of the laboratory and to respond to scientific and technological opportunities." It is the mechanism through which PNNL can support the formulation of new theories, hypotheses, and approaches; build new scientific capability; and identify and develop potential applications. The LDRD program is the principal mechanism for renewing capabilities within PNNL and bringing forward novel ideas that will become the next generation of science and technology. LDRD strengthens the Laboratory's fundamental research component, builds capability in support of our applied research and development programs, and translates scientific discoveries into technology applications. Specific objectives are to:

- Foster an environment that encourages creativity and innovation
- Fund novel ideas that have scientific/technical merit but that cannot be funded promptly through programmatic channels
- Investigate new ideas and concepts to the proof-of-principle stage
- Enhance PNNL's core capabilities, which are broad, enduring technical competencies upon which PNNL's reputation is based.

The projects supported by LDRD funding all have demonstrable ties to DOE missions. In addition, many of the LDRD projects are relevant to the missions of other federal agencies that sponsor work at the Laboratory. The program plays a key role in attracting the best and brightest scientific staff needed to serve the highest priority DOE mission objectives. The flexibility provided by the LDRD program allows us to make rapid decisions about projects that address emerging scientific challenges so that PNNL remains a modern research facility well into the 21st century.

Individual project reports comprise the bulk of this LDRD report. The Laboratory focuses its LDRD research on scientific assets that often address more than one scientific discipline. Though multidisciplinary, each project in this report appears under one of the following primary research categories:

- Advanced Sensors and Instrumentation
- Biological Sciences
- Chemistry
- Earth and Space Sciences

- Energy Supply and Use
- Engineering and Manufacturing Processes
- Materials Science and Technology
- Mathematics and Computing Sciences
- Nuclear Science and Engineering
- Physics

Each project report contains a project relevance statement, an introduction, a project description, and the results and accomplishments during the life of the project. Reports on projects continuing into FY 2010 should be regarded as progress reports; reports on projects completed in FY 2009 should be regarded as final summaries of the projects as a whole. This report also contains three appendices: Appendix A contains refereed publications (by author), Appendix B contains non-refereed publications and presentations (by author), and Appendix C contains a list of the principal investigators indexed to the document page numbers on which their report summaries may be found. In addition, a supplement (limited distribution, bound separately) includes new projects funded in FY 2010.

PNNL's LDRD Management Process

The major sequential steps governing the Laboratory's LDRD management process are summarized in the table below with more detailed descriptions following.

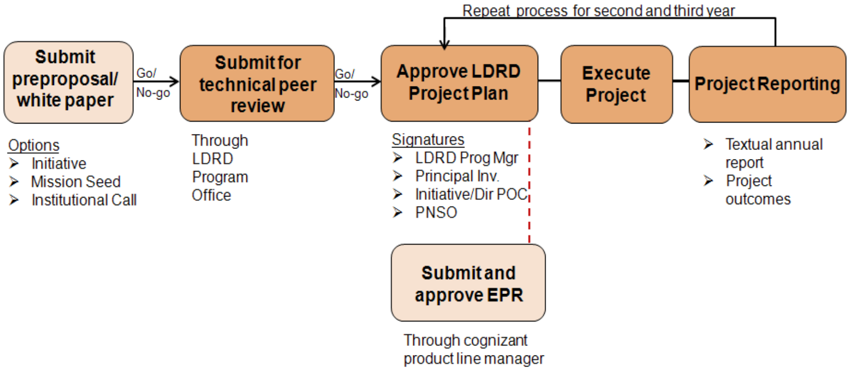
Month	Summary Schedule
October-February	Update of the Laboratory Agenda.
October-March	Deep dive (i.e., proposed new initiatives) activities are conducted.
April	Presentation of deep dives and mid-year evaluation of initiatives conducted.
May	► Annual Laboratory business planning guidance is prepared and issued. ► The Laboratory Director and Executive Committee approve initial funding for the LDRD accounts for the next fiscal year.
June	► Fourth-year project extensions (beyond the normal three-year time limit) are requested by initiative managers or directorate LDRD representatives to the LDRD Program Manager. ► Initiative managers and directorate LDRD representatives solicit LDRD proposals from research staff for next fiscal year.
Late June-early August	Initiative advisory committee reviews are held. Internal management reviews of mission seed and Laboratory Fellows projects held.
Late July	The LDRD program prepares and submits an annual LDRD program plan to DOE-SC. The LDRD program plan includes requests for a fourth-year extension of projects, and a list of potentially continuing LDRD projects into the next fiscal year.
August	Final advisory committee reports delivered to the DDST. These become the basis for guidance and funding considerations for continuing and new initiatives.
September	Principal investigators submit approved LDRD project plans to the LDRD Program Office for review of compliance with DOE requirements. An "electronic prep and risk" form is completed online by the principal investigator and signed by the appropriate product line manager.
September-October (and throughout the year)	The LDRD Program Manager forwards projects to the DOE-Pacific Northwest Site Office (PNSO) for review and approval. PNSO signs the project plan, and the LDRD Program Office releases funding so that work may begin.

Submission of PNNL's Annual LDRD Program Plan

DOE Order 413.2B requires that each multiprogram national laboratory submit an annual plan to the DOE-SC for approval of its LDRD program activities and funding levels for the next fiscal year. The LDRD program manager is responsible for the development of this program plan, which includes information about the Laboratory's current-year program goals, the broad scientific and technical areas planned for support, the maximum requested funding level, and requests for fourth-year funding of specific projects. In FY 2009, DOE approved PNNL's LDRD program at $31 million. Actual LDRD expenditures amounted to $29.4 million, or 3.3% of the Laboratory's operating funds.

Proposal Submittal and Signature Process

In FY 2009, 172 projects were funded through PNNL's LDRD program. The LDRD program office manages the process for proposal submissions and obtains the necessary approvals so that work can begin. This process is illustrated in the figure and includes the following major sequential steps:



LDRD Process Workflow

- For newly proposed projects, concept papers (or pre-proposals) are submitted for consideration for funding. A management review is conducted to determine if the project supports the major missions of DOE and capabilities of the Laboratory.
- For projects continuing from a previous fiscal year, project plans are updated and submitted to the LDRD program office.
- If a newly proposed project has been selected to go forward, a full LDRD proposal is completed and submitted to the LDRD program office for technical peer review.
- A final project plan is completed based on feedback from the peer review. After the project plan has been submitted to the LDRD program office, the project is routed for signature. When approved, principal investigators are notified that their research project can begin.
- Project work commences throughout the fiscal year. Technical progress and spending are monitored by the LDRD program office throughout the fiscal year.
- At the end of the fiscal year, each project reports on technical progress and completes project outcomes to the LDRD program office.

Details of the composition of projects and the peer review process are provided below.

Peer Review of LDRD Proposals

PNNL uses technical peer review to evaluate the quality, relevance, and performance of our scientific research. The Laboratory has a formal LDRD peer review process that ensures the technical integrity of our work, enhances our stature within the scientific community, and ensures that our research meets our customers' needs.

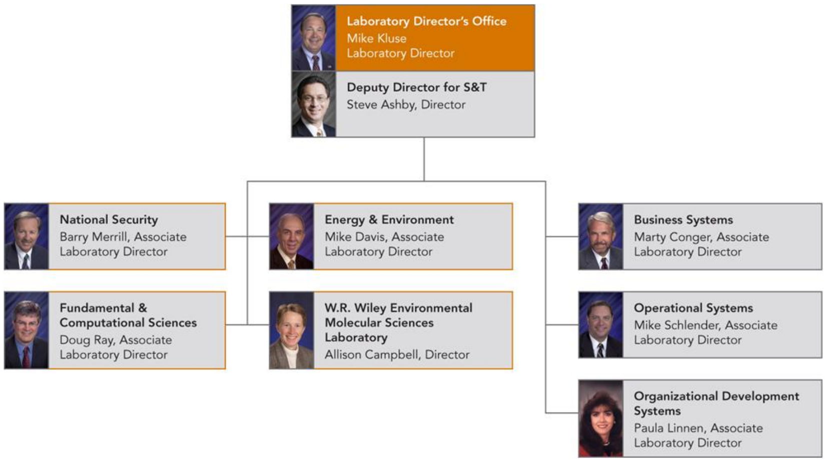
Overall, the Laboratory uses management review, internal technical reviewers, and external advisory committees in the annual review of LDRD projects. Each project is evaluated for mission relevance, scientific quality, and progress toward objectives. Midyear reviews and annual summaries of project performance are analyzed and linked to Laboratory critical outcomes. Project costs and spending rates are tracked in the Laboratory's financial system. Annual reports of technical progress are obtained from the principal investigators for annual reporting. Project performance outcomes are obtained electronically from each principal investigator.

The structure of PNNL's LDRD program and subsequent peer review of proposals consists of three separate components as described below.

- **Laboratory-Level Strategic Projects**. Laboratory-level strategic projects are directed at developing capability in support of the one of PNNL's 16 science and technology investment areas (called S&T initiatives). These projects are generally multiyear, multidisciplinary efforts. In FY 2009, PNNL's LDRD program funded 112 Laboratory strategic projects totaling $21.8 million and representing 65% of the total number of LDRD projects for the fiscal year. Projects in this category span research areas in systems biology, aerosol and climate science, catalysis, data-intensive computing and information analytics, materials science and technology, carbon capture and sequestration science and technology, and advanced nuclear science.

  Peer review of Laboratory-level strategic projects. In May, each initiative calls for pre-proposals that are reviewed by the initiative leadership (internal to PNNL), with a subset selected for potential funding. For projects that are selected for potential funding, an LDRD proposal is developed. The proposed new projects are reviewed by two or more internal PNNL technical experts for scientific and technical quality. The criteria used for rating the technical quality of project plans include intellectual merit of the proposed activity and broad impacts of the proposed activities.

  In addition to the internal technical peer review of each project, the Laboratory has an advisory committee for each of its initiatives. External experts review both newly proposed and continuing Laboratory strategic LDRD projects. Advisory committees review technical focus areas for alignment with DOE missions and needs and planning and execution. Each advisory committee forwards its final report and recommendations to the Executive Committee through the DDST. The Executive Committee reviews the recommendations, sets guidance, and allocates funding and other resources to the initiatives according to the strategic goals and priorities of the Laboratory. The initiative leadership and principal investigators are then notified of the funding decisions.



Executive Committee

- **Mission Seed Projects**. Mission-level seed projects, funded for one or two years, support near-term opportunities and mission needs of one or more of the three research directorates at the Laboratory. Ideas are submitted by individual researchers or small multidisciplinary teams. Projects are reviewed internally by subject matter experts, and at midyear, by management to assess progress against milestones. In FY 2009, 49 mission-level projects were funded, totaling $6.4 million, and representing 29% of the total number of LDRD projects for the fiscal year. Research topics under Science included panomics and biological research, radiation biology and biophysics, multiscale modeling of molecular reactions to catalytic reactors, microbial communities, climate change impacts, nanopartical interactions, computational fluid dynamics, petascale algorithms for molecular modeling, and ultra-pure nuclear physics materials, to name a few. Research under our energy portfolio included topics such as battery technology, carbon emissions, HVAC systems, solid state lighting research, marine biomass conversions, and grid technology. Environmental research included deep vadose zone remediation, carbonate geochemistry for sequestration of contaminants, mitigating the environmental impacts of tidal power, and process modeling of chemically complex solid-liquid suspensions. Lastly, we explored areas within national security, including nuclear fuel cycle safeguards, advanced radiation transport methods, holographic radar imaging, detection of biothreats, thermally stable chemical markers, smart sensors and analytics, portable actinide analysis, standoff radiography, and information fusion environments.

Peer review of mission-level projects. Each research directorate at the Laboratory conducts a review and evaluation process for proposed projects that address the directorate's mission objectives. The Associate Laboratory Director for each directorate appoints an internal committee to evaluate and recommend projects for funding. These internal review committees are also responsible for monitoring project progress and for overseeing the appropriate technical progress.

The LDRD program office also conducts a periodic review (usually every 2 years) of the mission-level processes. In addition, the directorate review committees review selected LDRD projects as a part of the directorate's strategy.

- **Laboratory Fellow Projects**. PNNL's Laboratory Fellows fund projects that are proposed independently by individual researchers and focus on mentoring young science and engineering staff with considerable potential for career distinction. Laboratory Fellows projects are reviewed annually and at midyear. Eleven projects were funded in FY 2009, totaling $1.2 million and representing 6% of the total number of LDRD projects for the year. Representative projects in this category include research on ion beam nanoparticle interactions, biotechnology, catalysis, advanced materials, radiation detection, photovoltaics, PEM fuel cells, and analysis of protein interactions to name a few.

Peer review of Laboratory Fellow projects. The review process for Laboratory Fellow projects is similar to that for the mission-level projects in that the reviewers are internal to the Laboratory. Laboratory Fellow projects undergo midyear and annual reviews by the Laboratory Fellow peers.

Compliance Review and Program Assurance

The LDRD Office and DOE-PNSO review and approve projects for compliance with DOE Order 413.2B. The oversight and reporting for the LDRD program is the responsibility of the LDRD Program Manager reporting to the DDST. As a part of the Laboratory's process for assuring compliance with DOE Order 413.2B, the Laboratory has developed an electronic system that houses all the project-related information. The system has been designed to manage the life cycle of projects from the technical review of a conceptual idea to the project outcomes that resulted from the funded research.

Advanced Sensors and Instrumentation

Advanced Environmental Sampling Technology for Safeguards and Proliferation Detection

Shane M. Peper, Norman C. Anheier Jr., Bruce A. Bushaw, David C. Gerlach, M. Lizabeth Alexander

◆ The overall goal of this project is to produce improved sample collection and analysis technologies for detecting proliferation signatures and to verify facility declarations in making determinations about the absence of undeclared nuclear activity. ◆

Environmental sampling is a critical verification tool for implementing safeguards and detecting proliferation activities. Samples are taken by inspectors who are granted access to a nuclear site under formal agreements. Advanced sample collection, sample analysis, and automated unattended monitoring techniques will be developed. Proliferation detection and verification of peaceful nuclear activities is a critical national security mission underpinned by sophisticated technology, which requires continuous capability improvements as existing threats grow and new threats emerge.

Our approach consists of three main tasks. First, we will develop improved sample collection methods and technologies for nuclear facility inspectors. Analyte, specific conductive films will be developed that can directly be deposited onto secondary ion mass spectrometry substrates, with the goal of significantly reducing the cost and time associated with laboratory analyses. Second, we will develop and evaluate a high resolution isotopic fingerprinting system for rapid screening of minor uranium isotopes (234, 235, and 236) at ultratrace levels. It is expected that minor isotopes can be directly quantified at femtogram levels and with abundance sensitivity below that achievable with conventional mass spectrometry. The unique selectivity provided by high resolution laser technique is expected to substantially reduce or remove complex sample preparation chemistry, resulting in faster analysis time. Finally, we will evaluate laser ablation, absorbance ratio spectrometry for highly enriched uranium detection within uranium enrichment plants. An automated, unattended environmental aerosol sample collection approach will be developed and combined with the uranium isotope ratio analysis system to detect enrichment facility misuse in a timely manner.

Progress on the first task included evaluating the use of advanced materials and methodologies for improving the collection and analysis efficiency of particulates. Several key procurements were made, including a LASAIR II 110 particle counter and a high-resolution epifluorescence microscope for spatially resolving particulates on the adhesive substrates under development. A postdoctoral fellow member of our team examined the coordination behavior of the iodide selective mercura-carborand ionophores using solvent extraction and a new phase transfer method under development. Additional progress in support of this effort has focused on obtaining several types of conductive polymers that are presently being evaluated for their efficacy as conductive substrates for direct analysis by secondary ion mass spectrometry.

Our second task evaluated the PNNL developed isotope selective laser ionization spectrometry for trace uranium isotopic profiling in environmentally collected samples. A new laser diode was installed in the external grating resonator cavity and was characterized for tunable single mode operation. The new diode delivers twice the output power, and test measurements demonstrated a signal to background greater than 1e6 for standard samples containing approximately 1 µg uranium. This is sufficient for profiling the natural isotopes (234, 235, 238) as well as ^{236}U arising from neutron irradiation in the nuclear fuels and weapons cycles. Standard large area air filter and surface swipe materials have been obtained and initial tests as substrates for environmental collection have been performed. Detailed comparative tests of these sampling materials and method optimization will be the first experimental studies we address during continuation of the project in FY 2010.

The third task evaluated the feasibility to adapt the PNNL developed laser ablation, absorbance ratio spectrometry into a uranium enrichment facility safeguards technology. A conceptual design for the laser ablation aborbance ratio spectrometry hardware and computer data acquisition system was developed. New automated data processing and enrichment analysis software was developed to convert raw absorbance signals into corrected enrichment ratio data. Significant technical progress was reported through several publications and presentations, including 1) a paper delivered to the Institute of Nuclear Materials Management 50th annual meeting in Tucson, AZ, 2) a refereed paper was compiled and submitted to *Spectrochimica Acta Part B: Atomic Spectroscopy*, and 3) a presentation abstract was submitted and a paper prepared for the International Atomic Energy Agency Workshop on Advanced Safeguards Technology for the Future Nuclear Fuel Cycle in Tokyo, Japan.

Circular or Full Polarimetric Holographic Radar Imaging for Tunnel and Explosives Detection

Douglas L. McMakin, Kyle J. Bunch, Gerald A. Sandness, Ronald H. Severtsen, David M. Sheen

◆ This project is developing a first-of-a-kind holographic radar imaging array using circular antennas in combination with three-dimensional holographic radar imaging systems for optimal tunnel and explosive detection. ◆

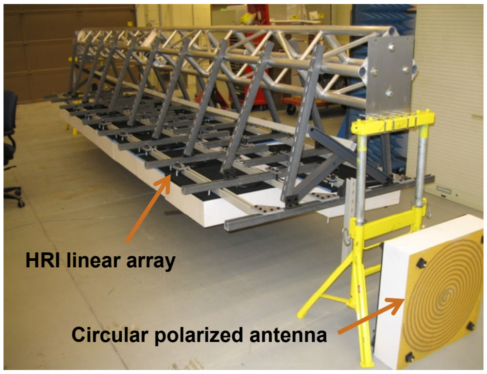
Tunnels used by terrorists to smuggle weapons and other illicit materials across borders continues to be a security challenge for the military and law enforcement. Conventional ground-penetrating radar systems perform optimally when they are in contact with the ground because it is much easier to couple electromagnetic energy from the antennas to the soil that way. However, dragging a ground penetrating radar system is not practical for improvised explosives device (IED) detection, and large area tunnel detection surveys may be impractical if natural impediments like heavy vegetation, large rocks, and logs have to be removed.

Antennas used on ground penetrating radar systems are typically linearly polarized, thereby making them limited in functionality and in the information that they can obtain. Circularly polarized antennas can be configured to receive either single or double reflection signals. This permits the removal of the strong surface reflection that is present if the radar antenna is not in contact with the ground. Circular or full polarimetric antennas configured as a linear array and combined with three-dimensional holographic radar imaging technology will provide an ideal sensor to detect tunnels and IEDs. Additionally, for tunnel detection, the polar diverse array and holographic radar can be mounted on a platform such as an aerostat (blimp) to hover over the ground to survey large areas of uncleared terrain.

The goal of this project is to develop polarization diverse (circular or full polarimetric) antennas that can be combined with a three-dimensional holographic radar imaging system for high performance tunnel and IED detection. These antennas will be used to fabricate a field deployable holographic radar imaging (HRI) array for detection and location of underground object. For tunnel detection, the frequency of operation will be in the 50 to 300 MHz range; and for IED detection, the frequency of operation will be in the 500 MHz to 2 GHz range. A key feature of the proposed system is that it can be mounted on a hover craft (aerostat) to survey large areas of unmanicured terrain in near real-time. These antennas will be designed and modeled on Ansof's high frequency structure simulator (HFSS), then fabricated and tested in combination with existing holographic radar transceivers.

In FY 2008, we designed, modeled, and fabricated circular polarized antennas for improvised explosive device and tunnel detection on HFSS at 0.7 to 4.0 GHz using a spiral design for improvised explosive device detection imaging and tunnel simulation imaging studies. We also designed, modeled, and fabricated 200 to 500 MHz spiral antennas for tunnel detection prototype. We conducted holographic radar imaging studies using 0.7 to 4.0 GHz transceiver on improvised explosive devices and simulated tunnels at various depths in the testbed covered with dirt. Additionally, we conducted holographic radar imaging studies on improvised explosive device command wires in dirt. Finally, we developed a preliminary design for holographic ground penetrating radar prototype imaging array.

In FY 2009, we used the 200 to 500 MHz spiral antenna design to fabricate a 2×8, 20 foot long HRI linear array prototype shown in the picture below. In the first implementation of this system, a trailer was designed and fabricated to mount and transport the HRI linear array for preliminary testing on the Hanford Site.



The 2×8 element HRI and one of the spiral antennas used in its construction. The HRI ground penetrating radar imaging system operates from 200 to 400 MHz.

Further work will focus on ground penetrating studies on underground structures and objects. We envision that a full capability will be a lightweight, field prototype, linear holographic array (2×8 elements) of 300 to 500 MHz circular polarized antennas mounted on a trailer that can either be pushed or pulled by a human operator or small ATV for rapid wide area surveillance, and preliminary three dimensional holographic radar ground penetration imaging results of simulated tunnels and explosives. We can then use this technology to survey buried nuclear waste sites and rapidly survey large other uncleared areas.

Complex Adaptive Sensor Systems

Mark E. Jones, Mitchell J. Myjak, John S. Rohrer, Jason C. Mount, Matthew W. Oesting;
George S. La Rue, Ding Ma, Dirk Robinson (Washington State University)

◆ This project has encompassed a number of initiatives to foster development of the next-generation sensor platforms for homeland security applications. We developed a compact, inexpensive electronics package to acquire and process data from dozens of sensors in parallel. Target applications for this work include radiation imaging and mass spectrometry systems. ◆

For certain homeland security applications, persistent monitoring systems are needed that can operate reliably with wide spatial coverage, near constant sampling, and within an environment characterized by rapidly changing conditions. These "smart" sensor platforms first acquire data from multiple discrete sensors or arrays of sensors. An onboard computational engine converts raw data into actionable information and determines the best course of action. The sensor platform then executes the action by issuing an alarm message to a command center or by alerting other nodes in a distributed sensor network.

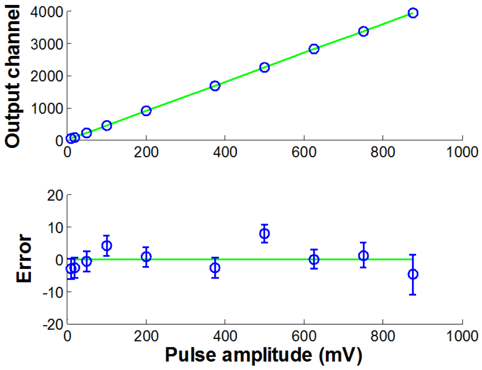
One critical need of a smart sensor platform is the ability to acquire and process data from multiple discrete sensing elements. Of special concern are one- and two-dimensional sensor arrays with large data outputs that when read in parallel offer significant benefits over checking each individually. For example, a position-sensitive photo-multiplier tube used for radiation imaging has a wire grid that collect position-dependent charge. Normally, wires are reduced to four terminals via a resistor divider circuit. However, reading out each wire removes resistor noise effects and improves energy measurement linearity. The sensor platform must have sufficient computational power to process sensor data to gain the benefits of parallel acquisition.

We developed a compact, inexpensive electronics package that can acquire and process data from 32 sensor inputs, which could be easily increased to over 100 using the same overall architecture. The electronics package consists of two circuit boards. A data acquisition board contains two custom integrated circuits developed under a PNNL/Washington State University partnership. Each integrated circuit contains a charge amplifier and two comparators for each of 16 inputs. The second circuit board is a commercial off-the-shelf development platform for reconfigurable computing. This data processing board contains a powerful field programmable gate array (FPGA), external memory, and various input/output interfaces. The cost of the two circuit boards is approximately $1000.

The electronics package offers flexibility to application developers. On the data acquisition board, users can specify the gain of charge amplifier by replacing an external capacitor. The system can measure sensor inputs in pulse or current mode, enabling the system tailoring to a wide range of sensors, including those used for radiation detection. The integrated circuit can handle positive and negative currents. On the processing board, the FPGA contains an array of reconfigurable cells and interconnection structures, along with a microprocessor core. Users can implement a complete computer system on one chip by mapping custom peripherals onto programmable logic around the central microprocessor. As expected, one peripheral is interface to the data acquisition board. The FPGA needs only two wires to communicate with each charge amplifier on the integrated circuit, allowing the system to process many sensor inputs in parallel. The micro-processor can then run custom processing routines to perform data processing tasks defined by the target application.

Test results demonstrate that the electronics package has all necessary functionality, acquiring data from the integrated circuit and even performing leakage current corrections of pulse-mode measurements. Measurements with a pulser indicate that the design achieves good linearity and precision. However, the initial version of the integrated circuit contains some design issues that limit its overall performance. Given the difficulty of designing analog integrated circuits, however, having a chip that functions on the first revision is a clear success.

A version of the electronics package is currently under development to support a mass spectrometry application for explosives detection. This system will contain 16 discrete channels connected to a segmented detector. The overall design is slightly modified to accommodate the ultra low currents encountered in this application.



Measured linearity and precision of one channel in the charge amplifier application specific integrated circuit. The top pane plots the output channel vs. input amplitude for a pulser input. The bottom pane shows deviation of the measured amplitude from the linear fit. The error bars indicate the one-sigma range of measurements.

Development of a Dual-Sided, Temperature-Controlled, Continuous-Flow Environmental Chamber

John E. Shilling, Chen Song

◆ As noted by the Intergovernmental Panel on Climate Change, the effect of airborne particles (aerosols) on climate remains a great source of uncertainty for climate models. Organic particles formed in the atmosphere, which are a large fraction of all atmospheric particles, and their life cycle are the foci of this project. ◆

Measurements show that organic aerosol particles comprise 20 to 90 percent of the total atmospheric aerosol burden. A significant portion of this organic mass (63 to 95 percent) is secondary organic aerosol (SOA), which forms in the atmosphere from gas phase precursors. However, state-of-the-art models currently underestimate measured atmospheric SOA concentrations by a factor of 8 to 100. The inability of models to reproduce measured SOA levels accurately illustrates an incomplete understanding of SOA formation and has important consequences for reducing the uncertainties associated with the effect of aerosol on global climate change. Therefore, insights into SOA formation and transformations, radiative properties, and the ability of SOA particles to form liquid water and ice clouds will directly improve predictions of global climate change.

Currently, most chemistry and transport models calculate SOA concentrations using the equilibrium partitioning theory coupled with experimentally determined SOA yield parameterizations. These laboratory based parameterizations are determined using environmental (smog) chambers, which simulate aerosol formation under controlled and well defined conditions. However, the parameterizations currently used by the models are based on experiments conducted with volatile organic compound concentrations, oxidant concentrations, and organic aerosol loadings far above those representative of the ambient atmosphere. Recent experiments have shown that these parameterizations cannot be accurately extrapolated to atmospheric conditions. In addition, many properties of the SOA such as density, chemical composition, and cloud condensation nucleus activity are central to modeling efforts and dependent on reaction conditions. Therefore, accurate representations of the SOA in models require data from laboratory experiments conducted under atmospherically relevant conditions.

In an effort to reduce these uncertainties, a new dual sided, temperature controlled continuous flow environmental chamber will be constructed to study SOA formation, evolution (aging), and the ability of SOA particles to act as ice nuclei and cloud condensation nucleus. The continuous flow design has several advantages over traditional chamber designs that allow experiments to be conducted under atmospheric conditions. Initial experiments conducted in the chamber will investigate the following: the link between anthropogenic and biogenic emissions in forming SOA, the yield and chemical composition of SOA produced from biogenic and anthropogenic volatile organic compounds under atmospherically relevant conditions, and the ice nuclei ability of SOA coated mineral particles.

Laboratory studies of SOA formation and subsequent processing have been carried out in environmental chambers for several years. However, due to limitations with the traditional experimental design, these studies were conducted using high concentrations of reactants that are not representative of the real atmosphere. It is becoming clear that data collected under these conditions cannot be accurately extrapolated to atmospheric conditions and are therefore of limited use to modelers. As an alternative to traditional experiments, we helped to develop the continuous flow environmental chamber. As a result and as noted above, experiments in continuous flow chambers can be conducted under atmospheric conditions, making extrapolations unnecessary. One early outcome expected from this project is the development of the continuous flow chamber capability at PNNL. This new capability will be used to conduct laboratory based research that is targeted at reducing the uncertainty associated with representing the SOA formation and processing in models. Data collected in these studies will be incorporated into climate models developed by PNNL to determine the effect of aerosol particles on climate change and to validate the models.

As a result of this project, a new temperature controlled environmental chamber capable of producing SOA under atmospheric conditions will be developed, characterized, and validated against literature data. Specifically, the dual sided chamber will consist of two Teflon bags coupled to the same gas handling manifold and analytical equipment, a configuration that will increase experiment duty cycle and reduce equipment down time. The chamber will operate primarily in a continuous flow mode, which produces a constant SOA output for analysis but will retain the ability to operate in the traditional mode. Operation of the chamber in continuous flow mode suppresses the loss of semi volatile species to the chamber walls, enabling lower, more representative concentrations of volatile organic precursors to be studied.

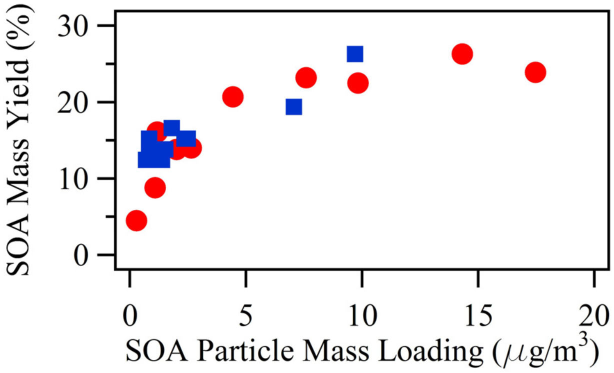
FY 2009 represented the first year of this project, and efforts were directed to the design and construction of the environmental chamber. This effort included some modifications to the laboratory space, including redesign of the power and climate systems of the building (e.g., compressed air, fume hoods, suitable laboratory space, vacuum lines, etc.). The majority of the chamber components were identified and purchased for installation. A full suite of analytical instruments required for the chamber measurements are now in use. A custom software program to acquire and store data from the instruments and sensors was written and successfully tested. An additional custom control program that allows the chamber conditions to be remotely controlled through a graphical computer interface was also written and tested. Together, these programs allow us to automate chamber operation so it can be reliably operated for week long time periods under the desired conditions with minimal supervision.

Because of some facility challenges, a smaller, more limited flow through chamber was been constructed so that scientific progress could be made concurrent with development of the state of the art chamber facility. We completed testing and validation of this secondary chamber and begun employing it for experiments probing possible synergistic interactions between organic compounds emitted naturally from plants and as a byproduct of human activities. The SOA yield from the dark ozonolysis of α-pinene has been measured for α-pinene concentrations of 1 to 16 ppbv and secondary organic aerosol mass loadings of 0.3 to 17.5 μg/m^3. These experiments demonstrate the ability of the chamber to produce secondary organic aerosol under atmospherically relevant conditions. The data agree well with literature data obtained under similar conditions, validating the chamber performance. Experiments investigating the secondary organic aerosol yield from cyclohexene ozonolysis have recently begun, where these data will serve as the baseline for further experiments employing mixtures of cyclohexene and α-pinene. Results and data derived from these studies will have important implications for the way aerosol particle formation is described in models.

Overall, the chamber will represent a new experimental capability at PNNL, enabling researchers to conduct laboratory studies of SOA formation and processing. The new capability will be an improvement over the current batch mode chamber in several key areas. First, implementation of the continuous flow mode has several advantages over batch mode operation (*vida infra*). These advantages include the ability to conduct experiments under more atmospherically realistic conditions, reduction in the influence of wall artifacts, decoupling of aging time from particle loading, and the ability to serve as a stable particle source for instrumentation or techniques with slow sampling rates. Second, temperature control will be added to the chamber, a critical capability in SOA research. Third, the ability to conduct photoxidation (OH initiated oxidation) experiments will be added to the chamber. The current facility is capable of utilizing only ozone as the oxidant, severely limiting the scope of possible experiments. Finally, an improved chamber manifold will be designed and implemented.

In FY 2009, collected and analyzed data have yielded two papers on this work. Published in *Atmospheric Chemistry and Physics*, the first paper showed that the chemical composition of secondary organic aerosol is dependent on the aerosol loading. In the same journal, the second paper showed that the ability of the aerosol particles to form cloud droplets is also dependent on the aerosol loading, as expected from our observations of the aerosol composition. A poster on the same work was presented at the American Geophysical Union fall meeting in San Francisco, CA.

After completion of chamber construction in FY 2010, we will spend time characterizing the unit and evaluating its performance. Initial experiments will focus on the formation of SOA from α-pinene photoxidation. Later experiments will build on this research and investigate the interaction of biogenic SOA with model anthropogenic particles. These results will provide the foundation for experiments employing authentic aerosol samples such as diesel exhaust and biomass burning aerosol. Our data will be incorporated into climate models developed by PNNL to determine the effect of aerosol direct and indirect radiative forcing on climate change.



Secondary organic aerosol particle mass yield from the ozonolysis of α-pinene. Data collected at PNNL in the newly constructed chamber are shown as circles. Literature data collected under similar conditions are shown as squares for comparison.

Development of a UF_6 Cylinder Integrated Portal Monitoring Capability

Michael M. Curtis, L. Eric Smith

◆ The objective of this project is to design conceptually and demonstrate the feasibility of a UF_6 integrated portal monitoring system to identify positively and verify the mass, enrichment, and movement date and time of 30B cylinders as they are removed from the process area of a uranium gas centrifuge enrichment plant. ◆

International Atomic Energy Agency (IAEA) inspectors spend an inordinate amount of time performing cylinder non-destructive assay activities during routine safeguard inspections at enrichment plants. All feed cylinders received and product/tails cylinders produced from the time of the last declaration (usually the day before previous inspection) are randomly sampled for verification together with a much smaller sample of static inventory. PNNL will automate cylinder verification activities to improve safeguards efficiency, positively identifying each cylinder and measuring its weight and enrichment. Efforts are directed principally to assay determination because it has historically proven difficult to automate.

In FY 2007, we focused on determining the correlation between enrichment and the neutron flux using sophisticated neutron transport codes. These models showed that the neutron flux tracks enrichment well within the IAEA's required measurement precision. The gamma ray flux was calculated for cross-comparison, resulting in a more robust enrichment measurement. While commercial operators may be reluctant to enrich uranium from spent nuclear fuel due to its significantly higher radiation dose, this component is required to implement nuclear fuel recycling using spent fuel reprocessing.

During FY 2008, a team took a series of measurements at the AREVA NP Fuel Fabrication Facility to estimate the variation in neutron and gamma ray source terms, collect detailed spectral measurements, and identify signatures typically not considered in agency measurements but capable of being collected using large volume NaI sensors with high energy collection efficiency. Validated by AREVA measurements, modeling was used to explore a broader cylinder parameter space and develop correlation and calibration curves to support quantitative performance predictions.

In April 2009, a team again took a series of measurements at the AREVA facility to support proof-of-principle analyses. A number of 30B cylinders spanning a wide range of enrichments were measured using the He-3 and NaI sensor package. The cylinder population spanned a wide range of enrichments and was diverse in terms of enrichment facilities that produced cylinders. A plot of neutron count rate versus ^{235}U mass for 11 product cylinders (2 percent enrichment) shows a linear relationship.

Measurement with NaI He-3 detector suite representative of integrated cylinder verification station instrumentation.

For optimal functionality, the integrated cylinder verification station requires a means of automated cylinder identification. One promising technique would employ the European Commission Joint Research Centre's Laser Item Identification System (L2IS), which reads cylinders using a laser scanner, creates an accurate three-dimensional surface reference model, and uses the information as a unique identifier.

Surveillance will be provided by the IAEA's pending Next Generation Surveillance System that will employ front end motion detection, MPEG image compression, authentication, and encryption. It will be used to verify system integrity, maintain continuity of knowledge on cylinders previously measured, and provide backup cylinder identification to the L2IS by photographing each cylinder nameplate.

The integrated cylinder verification station concept aims to automate cylinder verification activities and at the same time provide a more thorough nondestructive assay of cylinders (and consequently, greater sensitivity to anomalies and/or diversion scenarios). Research conducted in FY 2009 focused on developing the enrichment assay methods, since the complementary systems are either IAEA/Euratom-authorized equipment or commercial off-the-shelf instrumentation. Preliminary analysis of neutron and high-energy gamma signatures emanating from cylinders measured at an AREVA fuel fabrication plant indicate a strong correlation with the mass of ^{235}U in the cylinder—absolute mass, not just enrichment. Coupled to the traditional enrichment signatures (measured simultaneously by the same instrumentation operating in unattended mode), these new signatures hold the promise of accurately measuring unhomogenized cylinders and doing so in an automated fashion, key improvements over today's IAEA instrumentation.

Development of O-18 Isotope Ratio Measurements of Uranium Oxides and Surface Metal Oxides for Forensic Analysis

Douglas C. Duckworth, April J. Carman, Helen W. Kreuzer, James J. Moran,
M. Lizabeth Alexander, Matt K. Newburn

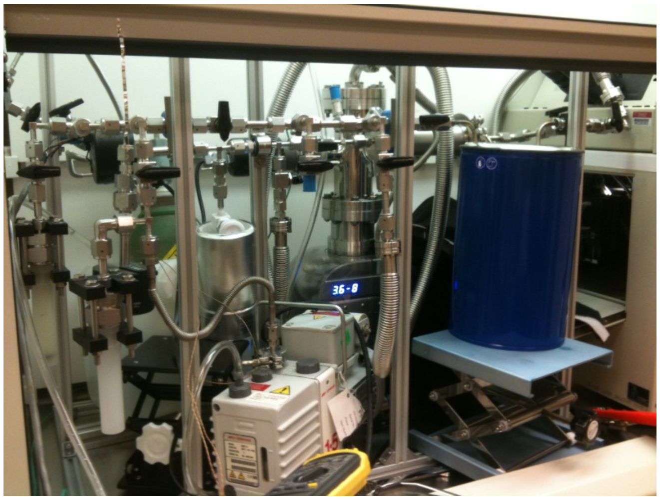
◆ This project promotes national security efforts by developing a methodology to exploit variations in isotopic composition that can reflect regional geographic differences or differences in material processing techniques. Our research intends to provide improved methods for precise and accurate oxygen isotopic compositions in nuclear materials and metal oxide surfaces. ◆

The goal of this project is to study the potential for laser fluorination to permit oxygen isotopic measurement on metal oxides, such as uranium dioxide in support of nuclear forensic applications. The measurement of stable isotope compositions is an increasingly active area of research. Stable isotope measurements of carbon, oxygen, nitrogen, and sulfur have proven to be useful forensic signatures in a variety of materials, including drugs, hair, food, and explosives. Defocused beam laser fluorination will be used to extend the approach to surface oxides for forensic analysis of materials including weapon components (e.g., uranium metal and improvised explosive devices). This system will build PNNL's capability in the area of forensic signatures in the processing and reprocessing of nuclear materials.

Regional differences in the isotopic composition of water are documented. Such regional variations in oxygen isotope content are dependent temperature and vary as a function of geographical latitude, elevation, and proximity to the ocean. Stable isotopes can also vary as a result of differences in industrial and chemical processes. Chemical and physical processes (e.g., evaporation, condensation, isotope exchange) can fractionate stable oxygen isotopes (^{16}O, 99.762%; ^{17}O, 0.038%, and ^{18}O, 0.200%) in water. Because water is a common solvent for uranium processing and reprocessing, isotopic variations occur in actinide metal oxides. Ultimately, stable isotope values of nuclear fuels and weapon materials should reflect that of the (regional) starting materials and isotopic fractionation resulting from processing variables such as temperature.

Laser fluorination-isotope ratio mass spectrometry (LF-IRMS) is the gold standard for oxygen isotopic analysis of various rocks and minerals due to the high precision (0.07–0.5 per mil) and accuracy that can be obtained. Due to the well-documented performance of LF-IRMS, this research focused on constructing an LF line to be interfaced with our dual inlet IRMS. Conversely, the conventional fluorination approaches involve heating refractory samples in a Ni reaction vessel at 600–700°C in the presence of fluorinating agents (F_2, ClF_3, and BrF_5). Incomplete conversion of the sample can result in isotopic fractionation and is not amenable to small sample sizes. In the early 1990s, focused carbon dioxide laser (10µm) heating were used to effect fluorination of refractory materials, allowing sample size requirements to be reduced from milligrams to sub-milligrams. The resulting reaction generated metal fluorides and oxygen gas that are collected for disposal and analysis, respectively. By defocusing the laser beam at a higher power, larger surfaces such as oxidized metal can be characterized. The application of LF-IRMS methodology to the study of uranium oxides and oxidized metal surfaces has not been reported in the extant literature and was the focus of methodological development within this effort.

This project resulted in the development and interface of a laser ablation system and fluorination line. A fluorination gas manifold sampling system was also developed for sample transfer to the IRMS. The laser ablation cell was designed and fabricated in house and interfaced with a commercial 266 nm laser ablation system. It provides a 10–400 µm spot size that has a highly defined ablation area. The system includes CCD camera for optical viewing of the ablated area and was tested with silicon wafers, demonstrating adequate desorption of oxide layers. Rather than direct coupling of the LF line to the IRMS, the system was redesigned, using a small commercial vessel for cryogenic collection. The system was completed and the sample collection "dry tested" by collecting oxygen from ambient air. Future work will focus on silicon oxide and uranium oxide sample analysis.



Integrated and operational laser desorption gas fluorination manifold system.

Distance-of-Flight Mass Spectrometry for Rapid, Portable Actinide Analysis

David W. Koppenaal, Charles J. Barinaga (PNNL); Steven J. Ray, Chris Enke,
Gary M. Hieftje (Indiana University)

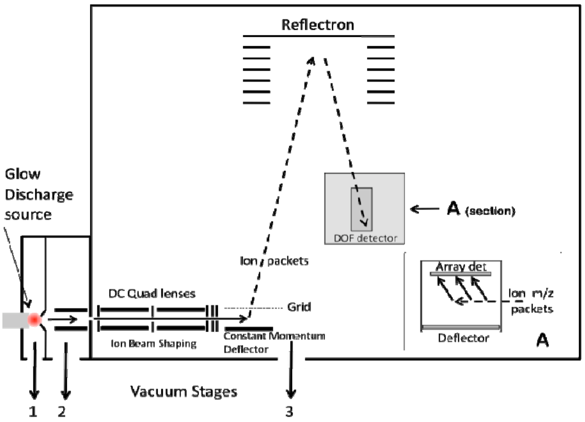
◆ A new approach to chemical analysis using the concept of distance of flight mass spectrometry (DOFMS) is proposed. This notion can provide characterization of nonproliferation samples and materials in a more cost- effective manner. ◆

We are taking a new approach to mass spectrometry using distance of flight to affect actinide isotope separation and detection. The concept is based on the premise that ions will separate according to mass/charge with transit in a field free region. Spatially separated or an array of detectors can be located along this path. At any given or selected time, the separated ion packet can be pulsed to this detector array for observation and detection. The ions are literally sorted by the distance traveled at a given time. This is in contrast to the more prevalent practice of time of flight, whereby ions are detected by arrival time at a fixed (and single) detector.

The DOFMS components consist of an ion source and ion optical elements, a field free region in which separation by mass to charge occurs, and an array detector with associated electronics and controls. Since there are no magnets, radio frequency fields, or sophisticated gating circuitry, instrumentation is amenable to simple, small packaging (laptop size for a small mass range) and portable operation. The DOF instrument concept can also be employed to collect physically on an analytical or preparative scale separated isotopes from complex mixtures. Isotope collection can be useful for preconcentration and subsequent matrix free analysis. For this project, we aim o develop a DOFMS prototype instrument, and demonstrate the concept, which has been only hypothesized and addressed theoretically.

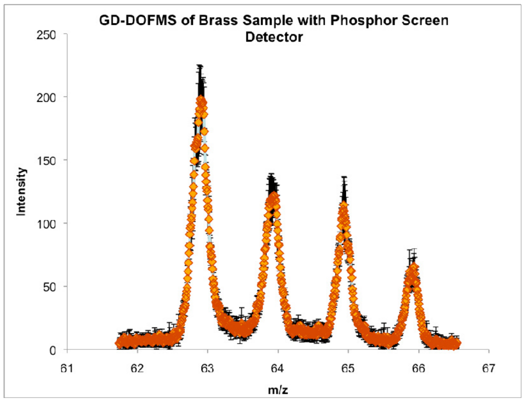
Results during FY 2008 included completion of modeling studies and construction of a prototype DOFMS instrument. Modeling and simulation of ion energies and trajectories were first run using a single ion mirror (reflectron) geometry instrument conceptual design for the DOFMS system. From this work, physical designs for ion optics and instrument layouts were developed. A design objective was to detect a mass range of 10 to 12 mass/charge (m/z) at a high mass range (i.e., actinide isotope mass range) across an array detector region of approximately 1 inch (typical of commercial multichannel plate detectors and direct charge detectors being developed).

The instrument design is shown schematically, and two prototype instruments were constructed from solid block aluminum stock using standard electrical discharge machining techniques. A glow discharge ion source was used in the initial DOFMS work. Ions extracted from this source are shaped (horizontally narrowed, vertically stretched) for pulsing using constant momentum acceleration into the field free reflectron region. The initial DOFMS detector used is a multichannel plate phosphor type detector but will change to a charge detector early in FY 2010.



DOFMS prototype schematic diagram. Section A shows ions extracted/pulsed to the array detector.

As noted, two prototype instruments were assembled, tested, and evaluated in PNNL and Indiana University laboratories, with both demonstrating empirical DOFMS separation and detection of ions. Model metal samples were used, with seminal DOFMS demonstration results for a brass sample shown below. Efforts during FY 2010 will include revision of DOFMS instrumentation platform, inclusion of inductively coupled plasma ionization options, and demonstration to high mass actinide and/or surrogate isotope analysis.



DOFMS spectrum of brass sample, showing copper and zinc isotopes.

Enhanced Isotope Ratio Measurement Capability

*Helen W. Kreuzer, M. Lizabeth Alexander, Daniel J. Gaspar, Jianzhi Hu, Bradley R. Johnson,
Robert A. Dagle, Nathan L. Canfield, Thomas A. Seim*

◆ The ability to determine the stable isotopic composition of small samples is important for signature characterization of materials related to weapons of mass destruction as well as the forensic analysis of such materials. We have developed a methodology that interfaces with existing isotope ratio mass spectrometers and permits stable isotopic analysis of samples 20 to 50 times smaller than can be measured with current technology. ◆

Chemically identical molecules can vary in their isotopic composition (for example, the relative proportions of deuterium [^{2}H] and protium [^{1}H] they contain. Therefore, the stable isotope ratios (for example, ^{2}H/^{1}H) of individual molecules and of bulk materials can distinguish otherwise chemically identical samples. The stable isotope ratios of manufactured chemicals are a function of those of the feedstocks used in the manufacturing process as well as aspects of the process itself. Similarly, the stable isotope ratios of biological materials are a function of the nutrients, water sources, and growth environment of the organism from which the material was derived. These attributes of stable isotopes present great potential for forensic as well as basic science, and make them a useful tool for combating the spread of weapons of mass destruction.

One obstacle to the exploitation of the power of stable isotopes is sample size. Current technology for the analysis of solids requires approximately 150 micrograms of organic material for oxygen and hydrogen isotope ratio analysis, and somewhat less for carbon. This amount may seem small but for the analysis of a single hair, for example, 2.5 to 3.0 cm is required. This amount represents between 2.5 and 3 months of growth; however, the use of a smaller sample size offers improved temporal resolution that could provide valuable information on a test subject's movements. Fundamental science applications such as the analysis of purified metabolites from microbial cultures or spatially resolved analysis of biofilms and forensic applications such as analysis of traces of explosives would be greatly facilitated by a reduction in the amount of sample required.

At project commencement in FY 2007, our design used laser ablation to remove small particles of solid sample and sweep them into a microscale reactor in a gas stream. In the reactor, particles are converted to simple gases and transferred to an isotope ratio mass spectrometer for isotopic analysis. The laser vaporization system was designed and tested using nylon (a polymer containing carbon, nitrogen, oxygen, and hydrogen) and horsehair as sample materials. We demonstrated that the particle size produced during the laser ablation was compatible with the reactor dimensions and large enough to avoid diffusion problems. No organic vapors were produced during laser ablation, which suggests that all organic material removed from the sample was converted to particles.

In FY 2008, we used scanning electron microscopy to evaluate the performance of the reactor coatings and found that graphite displayed superior performance. A major effort during this year was the development of a microchannel reactor using techniques developed and demonstrated in-house. Made from alumina powder and an aqueous binder-plasticizer system, the slurry was cast as a thin, flexible sheet called a "tape." One of the more significant challenges was to develop a technique to create a gas-tight bond between the different pieces of fully dense alumina. Several design criteria were critical to success of this bond method: it had to be stable up to 1400°C, chemically compatible with alumina (and bond without attacking it), leak tight, and have a similar coefficient of thermal expansion as alumina so the bond could survive heating and cooling without breaking. This problem was solved with the creation of a leak-tight pyrolysis temperature novel glass braze. The microchannel reactor bonded with the new sealant leak tight at 1400°C, and complete pyrolysis of butanol was demonstrated.

Our tests in FY 2009 show that laser ablation of 2 micrograms of sample generates enough gas for carbon and oxygen isotope analysis, fulfilling our goal of achieving a 50 fold reduction in the sample size required for measurement. Project accomplishments are as follows:

- We have shown that laser ablation of solid natural and manmade organic materials producing particles at the right size to move in a gas stream are of uniform chemical composition and not isotopically fractionated.
- We developed a new, process for bonding ceramic materials to make capillary reactors. The development of the reactor was described in a peer-reviewed publication.
- We have shown that our system enables isotope ratio measurement of samples 50 times smaller than those required by conventional technology.

Using raster controlled laser ablation devices, our approach offers the possibility of spatially resolved isotope ratio measurement.

Image Processing Methods Applied to the Detection of Highly Concealed Explosives

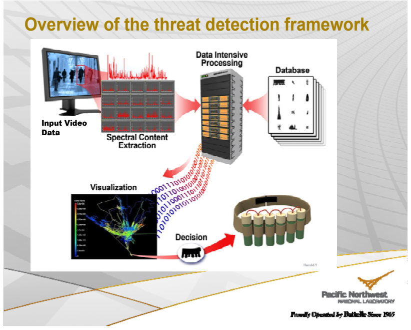
Harold E. Trease, Paul E. Keller, Brett G. Amidan, Ronald C. Taylor

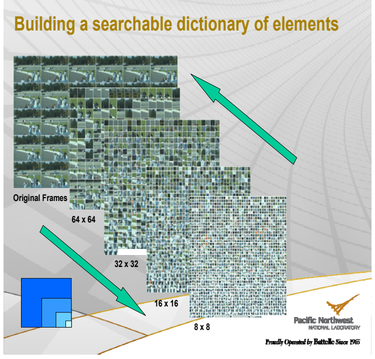
◆ This project is developing and applying advanced image and information processing algorithms for the detection of highly concealed explosives associated with security checkpoint screening technology. The research from this project will help produce the next-generation security surveillance and screening image systems. ◆

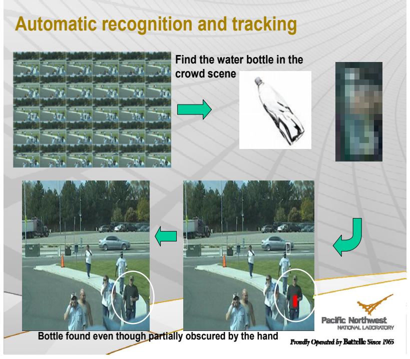
The detection of highly concealed explosives will require a multisensor approach that includes spectrometers, chemical sniffers, biosensors, three-dimensional imaging devices, and object recognition image processing software systems. Non-intrusive sensors allow data to be gathered and processed automatically, with the final step of the data analysis requiring a human being. A level of automation that integrates multiple sensor data requires that analysis be fast (in real and processing time) and accurate so that the chance of experiencing false positives and negatives is reduced.

The use of orthogonal and non-orthogonal sensors is important to reducing the false positive/negative detection rate. The most accurate and robust detection option lies within the image processing system that performs object recognition, clustering, classifying, and sorting. This will require sophisticated image and information processing algorithms and high throughput computing capability. The goal is to produce a computational framework that supports the analysis of multisensor data to produce a probability of detection of highly concealed explosives. The outcome of this project will be an image processing framework that takes as input from video to perform image segmentation, feature extraction, and feature classification, that feed into clustering, classifying, and sorting algorithms that ultimately produce a probability of detection for detecting highly concealed explosives.

The figures show the video processing framework and results of processing a test example using sparse representation algorithms to classify objects within a sequence of frames of video.


Overview of the threat detection framework


Building a searchable dictionary of elements


Automatic recognition and tracking

In FY 2007, we commenced writing algorithms for importing data from current millimeter wave imaging devices and building algorithms to process the data into a form that can be used by image processing and feature extraction algorithms. We wrote algorithms for building faceted surface representations of avatars (in the form of people) to address privacy concerns. We also performed computational physics modeling and simulation to investigate optimal standoff, spatial placement, or power requirements of individual imaging modalities or combinations of imaging modalities.

For FY 2008, we processed visible and infrared images/video and published our results. We developed and applied new image processing algorithms, writing to transform millimeter wave image data into faceted surfaces and tessellated volumes from which an isosurfacing algorithm extracted the external surface of the object. We used SafeView and Intellifit image data with and without various objects attached (guns, ammunition, and explosive charges) to test algorithms that highlight the differences that do not belong on normal human geometries, thereby identifying the concealed foreign objects. We tested algorithms that transform the millimeter wave data into faceted surface and tessellated volume. The resulting surface/volume mesh generated tables of area measures.

Progress made during FY 2009 involved a number of activities, including processing visible video, processing infrared images/video, and publishing results in presentations and papers. The main result of this work has been the development and implementation of new image processing algorithms that discover hidden objects or hide sensitive personal features from data collected using next generation security checkpoint imaging devices (SafeView and Intellifit) used at airport security checkpoints.

Instrument Control for the “Next Generation” Proteomic Measurement Capabilities

Mikhail E. Belov, William F. Danielson III, Yehia M. Ibrahim, David C. Prior, Richard D. Smith

◆ This project is developing a significantly improved capability for proteomics measurements that can be applied to a suite of biological and environmental research problems. ◆

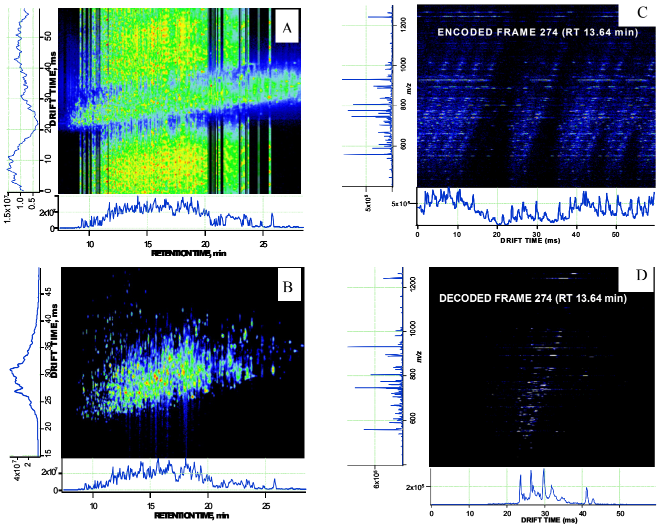
Proteomics is rapidly becoming an essential tool for biological research, enabling new “systems biology” approaches for the discovery and validation of disease biomarkers and environmental perturbations. Enormous sample complexity and biological variability are best addressed with high-throughput, high-sensitivity instrument platforms based on multi-dimensional separation approaches.

In a number of biochemical applications (including experiments aimed at discovery of candidate biomarkers in human blood plasma for early cancer detection), many proteins of interest are expected at abundance levels far below that of higher abundance proteins, representing a significant analytical challenge for multi-dimensional separations. An elegant and highly efficient approach for increasing the sensitivity of a proteomics platform is to incorporate orthogonal and complementary separation stages. A combination of fast reverse-phase capillary liquid chromatography (LC), gas phase separation, such as ion mobility spectrometry (IMS), and time-of-flight mass spectrometry (TOF-MS) provide a basis for detection and reliable identification of candidate biomarkers, as well as additional criteria for the enhanced screening and differentiation of disease states. Such a complex three-dimensional separation platform requires intelligent computer control of the statically and dynamically operated components, software communication between different parts of the system, and precise experimental timing determined by hardware triggers. This research is focused on the development of intelligent instrument control capabilities for the next generation LC/IMS TOF-MS proteomics platform.

Project efforts have included the development of a basic control system for a high-speed platform, allowing the automated selection of analysis and data acquisition parameters. A computational capability for real-time data processing and display was developed to handle the extremely high rate of data generation by the new instrument platform (~100 Mbytes/s). The data handling capability was complemented by development of a core set of informatics tools, allowing identifying and quantifying proteins in a complex biological matrix and the extraction of useful biological and chemical information from these large data sets.

Several key features included a fully automated, highly robust, sensitive instrumentation capable of performing three-dimensional analysis of biological samples in 20 minutes, with a total number of analyses per day exceeding 80. Sensitivity and dynamic range of the novel platform were superior over those of the more conventional (longer) capillary liquid chromatography separation-high resolution mass spectrometry systems. In addition to the commonly used chromatographic and mass spectrometry domains, the platform enables mobility-assisted separation and identification of bio-molecules based on their structures so that isobaric components with similar hydrophobicities and different biological functions are amenable to detection.

In FY 2009, several instrument control/data processing capabilities were developed and implemented. A four-column liquid chromatography instrument was programmatically linked to IM/TOF mass spectrometer through a component object modeling interface using robust communication protocol. This resulted in staggered condensed phase separations characterized by zero dead time between data acquisitions in adjacent chromatographic runs. On-line liquid chromatography was coupled to dynamically multiplexed ion mobility separations, resulting in an instrument duty cycle of greater than 50 percent throughout each chromatographic run. A key feature of the dynamically multiplexed system is the ability to track down variability of an ion source and adjust instrumental parameters (ion accumulation time, IM encoding sequences, etc.) to ensure high duty cycle (more than 50 percent) and linearity of the detection system. Highly efficient collision induced dissociation downstream of the ion mobility separation and the novel algorithm for deconvolution of the multiplexed fragmentation spectra were developed and evaluated with complex proteolytic digests.



On-line capillary reverse phase liquid chromatography/dynamically multiplexed IM-TOF mass spectrometry of a depleted human blood plasma sample: A) encoded IM/retention time map, B) decoded IM/retention time map, C) encoded TOF/IM frame corresponding to retention time of 13.64 min in A), and D) decoded TOF/IM frame corresponding to retention time of 13.64 min in B).

Metal Beta-Diketonate Polymers for Selective Concentration of Explosives

Scott D. Harvey, Thomas J. Wenzel

◆ We are investigating the ability of metal β-diketonate polymers to concentrate explosive vapors selectively, resulting in a relatively pure, concentrated sample for further analysis. This capability will enable design of streamlined field-portable instruments that can effectively detect small amounts of explosive materials present in the air. ◆

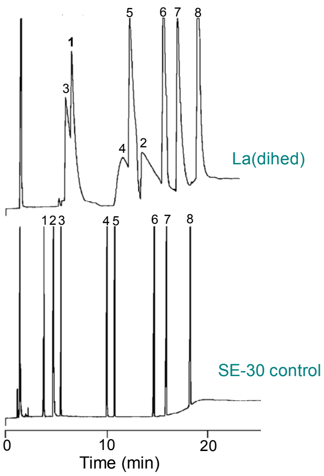
Previous researchers have described selective capture of alcohols and amines (Lewis base analytes) on metal β-diketonate polymers (Lewis acidic polymers) from complex samples. We are investigating the gas-phase interactions of metal β-diketonate polymers with explosive materials. Although not previously studied, interactions between metal β-diketonate polymers and explosive materials might be expected because of the basicity of the nitro group. Chromatographic studies quantitatively investigated the polymer/explosive-interaction strength and selectivity (i.e., the ability to discriminate against matrix background interferences). Metal β-diketonate polymers were then incorporated into other analytical formats and evaluated to determine their trace-level analysis capability.

Activities in FY 2008 focused on using packed-column gas chromatography to examine the affinity and selectivity of metal β-diketonate polymers for various explosive material classes. Chromatographic capacity factors were used to demonstrate strong gas-phase interactions for various explosive types. To be useful, analytical materials must discriminate against non-polar hydrocarbons, which constitute the major organic matrix interference found in air. To address this constraint, the Kováts index was used to demonstrate quantitatively high selectivity of metal β-diketonate polymers toward TNT relative to *n*-alkanes. The combination of high affinity and selectivity make these materials ideally suited for select concentration of explosives.

Other studies examined selective capture of explosive materials on solid-phase microextraction (SPME) fibers coated with a metal β-diketonate polymer [the La(III) complex of *p*-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene, La(dihed)] compared to a poly(dimethylsiloxane) (PDMS) control. The PDMS and La(dihed) fibers were placed in an explosives storage bunker, where the air was simultaneously sampled for 48 hours. Fibers were analyzed in the laboratory using GC/MS techniques coupled with selected ion monitoring. The PDMS control fiber captured 2,4-dinitrotoluene (2,4-DNT) at the detection limit of 1 picogram with no indication that TNT was present, whereas the La(dihed) fiber captured nine times more 2,4-DNT and enough TNT to give a strong signal. This result is significant because sampling with the La(dihed) fiber readily detected TNT, an analysis that cannot be achieved using traditional SPME approaches. The study is relevant because it demonstrates detection of TNT in a realistic environment at the low concentrations (< 3 parts-per-trillion) required to detect hidden explosives.

Studies in FY 2009 focused on preparing capillaries coated with metal β-diketonate polymers as stationary phases. The goal of this work is to coat multi-capillary columns (MCC) and use a short (i.e., several cm long) segment of the MCC to concentrate samples selectively. After sampling, the MCC would then undergo precise thermal elution to yield narrow sample fractions for further analysis. This work required development of a novel static capillary-coating technique that uses a low-boiling-point binary azeotrope that contains methanol. With this procedure, we prepared lanthanide(dihed)-coated capillary columns and demonstrated their selectivity toward explosive materials and related analytes. These experiments compared retention of a test mixture containing 1-nitrobutane, cyclohexanone, *n*-pentyl nitrate, 2,3-dimethyl-2,3-dinitrobutane, 4-nitrotoluene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, and 2,4,6-trinitrotoluene under identical conditions between lanthanide(dihed) columns and an appropriate control. Upcoming work will involve coating small diameter columns bundled in the MCC format.

We also demonstrated selective explosive vapor sampling on a deactivated quartz-fiber filters impregnated with Cu(dihed) polymer combined with direct detection by ion-mobility spectrometry. This approach has potential for field portability, but because of radical analysis simplification, some capability limitations exist. Related experiments demonstrated gas-phase uptake of the non-volatile explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (i.e., RDX) for the first time.



Chromatograms of explosives-related test probes showing selective retention on a capillary column coated with a mixture of La(dihed) polymer combined with SE-30 (top) compared with a control column coated only with SE-30 (bottom).

Multi-Modality Sensing Platform for Smart Detection of Explosive Traces

Liang (Frank) Wang, James S. Swensen

◆ It is important and advantageous to develop a sensing platform of multiple transductions in concert for early detection of powder or vapor phase explosive molecules and discrimination of target analytes at extremely low concentrations. This project will ultimately lead to a selective, sensitive, portable, cost-effective sensor device for remote explosive recognition that has high impact on national security in preventing potential terrorist attacks. ◆

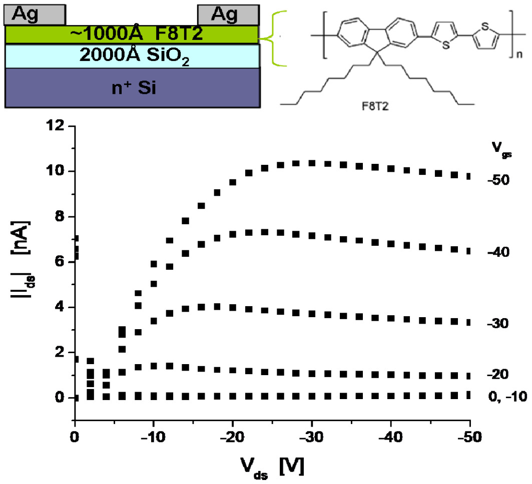
Organic field effect transistors or chemi-resistors have been widely used as chemical sensors with sensing signals retrieved from the changes in the bulk or channel conductance upon exposure to an analyte. These types of sensors have gained increasing interest due to their portable size and ease of fabrication, the availability of modifying molecule/polymer structure for sensing specific targets, the simplicity of sensing signals for real time readout and data process, and their widely accessible sensing area. However, the response of these sensors only accounts for a single physical property such as the amount of charge or dipole moment carried by the analyte, thereby limiting their distinguishability.

We aim to provide a new architecture for chemical sensors built on a light-emitting organic field effect transistor, targeting early and real-time detection of explosives with improved selectivity and sensitivity. The scope of the work involves fabrication of an operational light emitting organic field effect transistor-based sensor and demonstration of its enhanced performance in sensing simple, vapor phase explosive molecules. The sensing response will be read not only from the electrical current but also simultaneously from the light emission, which brings an additional and synergic capability of transduction to distinguish target analytes at extremely low concentrations. By examining various physical properties of the device such as spectral and temporal analysis, this project will also investigate the interaction between target analytes and the transduction elements including the channel materials and interfaces in a light emitting organic field effect transistor. These studies will enable the fundamental understanding of the sensing mechanism and pave the way to a selective, sensitive, portable and cost-effective sensor for explosive detection to prevent potential terrorist attacks.

A sensing system has been completed with analyte vapor delivery in precise control and capability for signal measurement while the device is exposed to the explosive target. We have built a sensing chamber to provide a clean environment before the introduction of analyte vapor. The analyte 2,3-Dimethyl-2,3-dinitrobutane, a detection taggant for explosives, will be filled into the system with fine adjustment to the flux of analyte vapor. A heating tape is provided for facilitating the sublimation of analyte and supplying enough analyte flux.

An organic field effect transistor has been fabricated and characterized, which demonstrated gate modulated hole transport. Gate modulation was observed on hole transport through the channel with mobility of 9×10^{-4} cm^2/V·s, comparable to values reported in literature: 0.5-8×10^{-4} cm^2/V·s. However, no electron transport was observed in these devices, mainly because electron injected from drain electrode was soon quenched by oxygen or water molecules while testing in air. We have searched the literature and found a recent report of light emitting organic field effect transistors using an air stable material with high mobility that can emit observable amount of light when it was operated in air.

Eventually, we will expand the breadth of the existing integrated organic/inorganic thin film deposition capability at PNNL and result in new capability to fabricate chemical sensor devices and perform sensing characterization in a unique way of time resolved electrical and optical measurements. We expect to publish the fundamental knowledge generated from these studies in high impact journals and present the results in national conferences and workshops. During FY 2010, we will deliver the prototypical light emitting organic field effect transistors device and use it as a sensor. We will also try different types of organic semiconductor as the channel material for their sensing response to a group of explosive analytes.



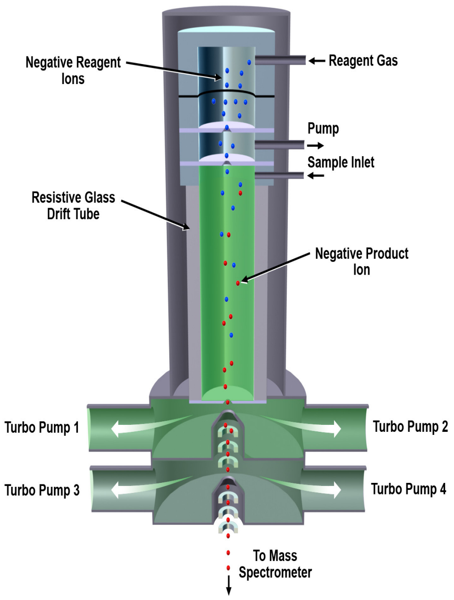
Device structure and electrical characteristic of the fabricated light emitting organic field effect transistor, showing gate modulated hole transport.

Rapid, Sensitive and Selective Explosives Detection Using Tunable Chemical Ionization Drift Mass Spectrometry

M. Lizabeth Alexander, Brian H. Clowers

◆ We propose to modify existing field-portable proton transfer reaction mass spectrometry instrumentation with the addition of new ionization. This non-radioactive source promises to extend the high sensitivity and rapid time response of chemical ionization drift mass spectrometry to the real-time detection of explosives and related compounds critical to national security. ◆

Proton transfer reaction mass spectrometry (PTR-MS) is a specific example of chemical ionization drift mass spectrometry (CIMS) that has been widely demonstrated as a highly sensitive and specific technique for the rapid detection of trace levels of volatile organic compounds in the atmosphere. Unfortunately, the energetics of the proton transfer mechanism used in PTR-MS are not favorable for detecting important gas phase species indicative of explosives or other threat agents. The high electronegativity of these signature compounds makes them ideal candidates for selective ionization with alternative particularly negative ion chemical agents. Our proposed ionization source and the sensitivity, specificity, and rapid time response of the new technology are applicable to a wide range of national security requirements, including facilities monitoring and protection, emergency response, and source attribution.



Schematic diagram of PTR-MS high-sensitivity source and interface.

The distributed plasma ionization source (DPIS) will be incorporated with the custom PTR-MS instrumentation designed and built to minimize the level of instrument development required and allow demonstration of the basic concept. This will allow efforts to be directed toward investigation of gas phase ion chemistries to obtain the necessary fundamental understanding required for future instrument design. PTR-MS chemical ionization drift mass spectrometry instrumentation has been repeatedly demonstrated as portable and robust in field measurements of volatile organic compounds in the atmosphere. Following demonstration of negative ion generation using the DPIS at reduced pressure but before examining complex mixtures of explosives with potentially interfering background compounds, the negative mode gas phase kinetics of explosives with the range of negative reactant ions produced by the DPIS will be performed. The final stage of the project will demonstrate the method detection limit improvements compared to traditional IMS systems equipped with the DPIS. Scientific and technical insights gained from these basic studies will be used to develop preliminary design specifications for a new CIMS platform for the detection of explosives with state-of-the-art sensitivity and selectivity.

This project began in June 2009, and we focused efforts on the redesign of the new high-sensitivity PTR-MS to allow routine operation for either positive or negative CIMS. This would also allow a dedicated instrument for the current and related projects. The ion optics and voltage biasing schemes were redesigned, and additional power supplies and other parts were procured. A SIMION model was constructed to produce ion trajectories and establish optimal potentials for both positive and negative CIMS. This model will be expanded in FY 2010 to include the variability in pressure through the ionization and extraction regions. The fully functioning instrument will be used to:

- Evaluate the utility of GC-PTR-MS for explosives detection.
- Establish the parameters under which negative ions from the DPIS may be produced at reduced pressure (e.g., less than 10 Torr).
- Demonstrate operation of PTR-MS in negative ion CI mode using a suitable explosive simulant compound.
- Demonstrate state-of-the-art detection limits for a range of common explosives.
- Characterize the ionization and reaction kinetics and mechanisms for negative mode CIMS for compounds relevant to explosives detection.
- Develop preliminary design specifications for a fieldable chemical ionization drift mass spectrometry platform capable of analyzing chemical classes with a high degree of specificity that respond to both positive and negative mode ionization.

Real-Time In Situ Millimeter Wave Sensors for Gasifiers

S. K. Sundaram, James E. Cabe, Douglas J. Reid, Mark D. Bearden, Stanley L. Owsley Jr.

◆ Millimeter wave sensor technologies developed for the in situ measurement and verification of slag characteristics are important for proper control of coal gasifiers and impact three critical performance areas: temperature profile inside the gasifier, refractory corrosion monitoring, and slag viscosity. ◆

With variable crude oil prices, the conversion of coal into clean burning liquid fuel offers an economic, environmental, and security solution. For several reasons, the benefits of gasification technologies for solid feedstocks have not yet been leveraged. One of the major technology issues is an advanced sensor for gasifier operation and control. Previously identified sensor needs are both the physical (temperature, solid flow, flame quality, and pressure) and diagnostic (corrosion, component degradation, self diagnosis, and refractory contouring) measurements. According to the Vision 21 Technology Roadmap, sensors based on new approaches and technologies need to be developed in the next five years, tested in situ in real time and in operating plants, and demonstrated in a "smart plant" within the next 10 to 15 years. In spite of the National Energy Technology Laboratory's efforts in this and other gasifier areas, most power plants are not presently equipped with state of the art sensing capability, and sensors are not currently available to meet Vision 21 plant needs.

Millimeter waves of electromagnetic radiation in the 30 to 1000 GHz range are ideally suited for remote measurements in the harsh environment of gasifiers. Millimeter waves are long enough to penetrate optical/infrared obscured viewing paths through dust, smoke, and debris commonly encountered in gasifier environment but are also short enough to provide spatially resolved point measurements for profile information. Another important advantage is the ability to fabricate efficient millimeter wave gasifier viewing components from refractory materials. Some of the refractories and alloys from which gasifiers are constructed can be used to fabricate millimeter waveguide/mirror components that go into the gasifier for long life survivability.

We propose to build upon this technology to develop a remote sensor system to sense several parameters that are important to efficient and cost-effective operation of the gasifiers. The specific objectives are to 1) use existing millimeter wave sensor technology to measure gasifier temperature, slag viscosity, and refractory corrosion, 2) demonstrate proof of principle measurements of these parameters, 3) design, build, and test an integrated prototype to measure the parameters, and 4) demonstrate the sensor technology in a gasifier testing facility. A basic experimental system will be assembled for measuring these parameters for gasifier applications to obtain the initial data using selected refractories and slag chemistries. Once proven, an integrated sensor will be designed, tested, and demonstrated in a prototypic gasifier.

The development of the PNNL gasification and carbon capture test facility capabilities is intended to provide a platform that enables continuing research into clean coal technologies, carbon capture, and ancillary technologies such as the millimeter wave sensors. The conversion of coal into clean burning liquid or gaseous fuels offers a viable solution to reducing the traditional emissions associated with the combustion of coal, while providing a demonstrated pathway to the capture of CO_2. The benefits of research level gasification technologies for solid feedstocks have not yet been adequately leveraged due to several drivers. Of the primary issues limiting development is simply the sheer size, lack of operational knowledge as it relates to the durability of materials, and lack of operational flexibility.

The engineering scale facility was commissioned with the expressed intent of providing realistic operating conditions and syngas to a variety of downstream processes under evaluation. Due to its size and flexibility, the gasifier may be operated in fuel rich combustion, oxy combustion, and precombustion modes, depending on the needs dictated by operational targets and the downstream processes being evaluated. The process for accomplishing these objectives followed a prescriptive methodology starting with mechanical completion and development of a Safe Work and Standard Operating Procedure, first fire and ensuing gasification associated with liquid fuel(s), and finally the atmospheric gasification of pulverized coal.

During FY 2007, we made significant progress, including the ability to differentiate refractories and slags, as samples showed high emissivity with distinct temperature dependence. We measured the dielectric properties and transmission of 20 slags prepared at PNNL and five refractory samples relevant to U.S. coal industries. Results were used in selecting frequencies and designing hardware (waveguide, lens, and detectors) for millimeter wave sensor development. Additional data collected on selected non oxide materials have shown promise. We established and tested a dual receiver diagnostics system for high temperature measurements in simulated gasifier environments for capability development. The millimeter wave system was interfaced with a novel research gasifier using a flange system.

Continuing our research in FY 2008, the following proof of principle tests were completed: 1) slag penetration into the refractory, 2) viscous flow of the viscosity standard fluids along the alumina slab at room temperature, and 3) viscous flow of the viscosity of slag along the refractory wall at higher temperature. Having been evaluated on a bench-scale level in FY 2008 and early FY 2009, the intent to demonstrate millimeter wave sensor technologies' effectiveness on an operating entrained flow gasifier required the full commissioning and operation of an engineering scale gasifier. The majority of continuing project activities were thus focused on this aspect.

For FY 2009, gasifier commissioning activities included operating the gasifier for initial bake out of refractory and eight total sustained runs using liquid fuel (methanol and diesel). Key objectives met included full mechanical check out, verifying and updating the Safe Work and Standard Operating Procedure, and documenting system safety environmental controls. Heat loss calculations were recalculated using data from operations (fuel feed, thermocouple readings, shell temperatures, and kilowatts for heating element) to evaluate expected conditions as the unit came to equilibrium.

Four preliminary runs were conducted feeding both methanol and dry pulverized coal; the longest runs were less than 1 hour, at which time the pulverized coal feed mechanism plugged. Changes to the feed system were made to place slight positive pressure on the fuel supply system (coal) and to reduce the impact of atmospheric coal feed into the burner. This required a change to the burner layout that can currently accommodate concurrent feeds of both liquid and pulverized coal through separate feed locations. Ensuing runs were of several hours in length and produced enough syngas to begin capturing for use in bench level testing of carbon capture and ancillary technologies that require a stable delivery of coal derived syngas.

During FY 2010, we intend to focus the project on three primary objectives, as described below.

- *Continuous operation with improved safety and material delivery*. Our first objective will be to extend the continuous run time of the gasifier by using positive displacement fuel feed mechanisms and use of mass flow control for density evaluation. Primary emphasis is on improved design, reliability, and safety by transitioning away from passive coal feed protocols. This will also advance modeling accuracy, as we expect to have a much higher degree of rigor applied to the fuel feed measurements (btu per hour).
- *Improved fixed carbon conversion*. By relining the gasifier, we expect to operate at higher internal (refractory face) temperatures improving overall fixed carbon conversion. During the process of commissioning the unit, it had been determined that a less tolerant refractory liner was initially placed into service for expediency. A more temperature tolerant refractory has already been selected for liner replacement. Relining the gasifier will also enable the placement of millimeter wave sensor line of site channels.
- *Integration of research projects for syngas utilization and carbon capture technologies*. The integration of research project(s) are expected to advance core initiative objectives directly based on syngas and flue gas utilization, including millimeter wave sensors, independent water gas shift reactor, solid oxide fuel cell evaluations, and hot gas clean-up.

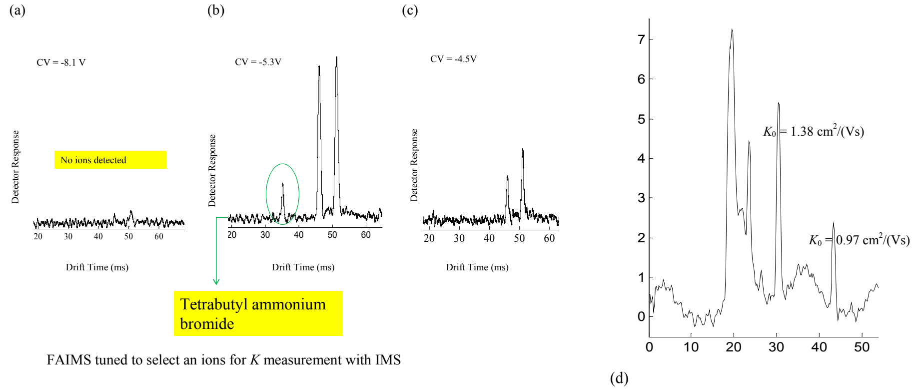
Sensitive and Specific Detection of Explosives Using a Multiplexed Two-Dimensional Field Asymmetric Waveform Ion Mobility Spectrometry/Ion Mobility Spectrometry System

Alexandre A. Shvartsburg, Mikhail E. Belov, Brian H. Clowers, Richard D. Smith, Keqi Tang

◆ This project will create a new ion mobility spectrometry (IMS) based capability for explosives detection that will improve analytical performance by an order of magnitude in terms of specificity at equal sensitivity or sensitivity at equal specificity. ◆

Present IMS systems for explosives detection suffer from sensitivity and specificity limitations. The need for higher sensitivity is pressing and essentially open ended. While it has been discussed at length in scientific terms, a general illustration is that government scientists who work on explosives detection using IMS and routinely handle explosives on the job are often able to board commercial flights unimpeded. The need for greater specificity is also high, considering the business disruption, financial costs, and potential legal implications of false positive identifications of explosives within modern transportation and other civilian infrastructure. With present detection systems, such false positives are common.

During FY 2007, we designed a new FAIMS/IMS operating system. The system was assembled and fitted with electronics/control hardware. We modeled various aspects of FAIMS separations using previously developed simulation software. Our aim was to explore new design concepts and optimize parameters that control FAIMS performance in general and for explosive detection specifically. We simulated the field driven FAIMS and characterized its performance fundamentals. The major advantage was a great reduction of discrimination based on absolute ion mobility or diffusion coefficients relevant to all global analyses, including explosives detection.

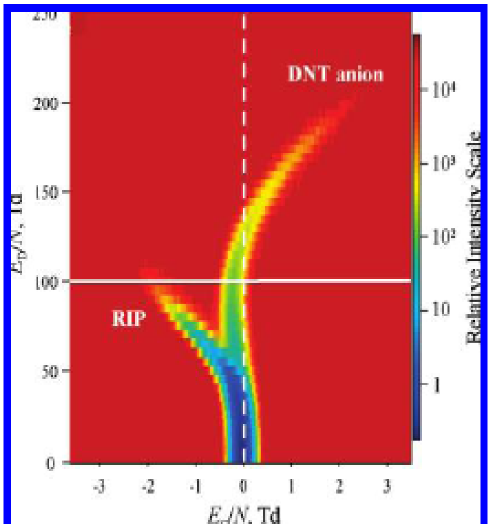


Drift-tube IMS analyses of ions after FAIMS filtering. IMS spectra at 3 CV values: (a) baseline, (b) species of interest (TBA ion) and other ammonium bromides, (c) other ammonium bromides only. In (d), we show the IMS spectrum for RDX (obtained with FAIMS in the all-pass mode) using a multi aperture FAIMS inlet; with the circular inlet no signal could be discerned.

In FY 2008, we completed construction of the system. Once hardware assembly was finalized, the project satisfied PNNL safety regulations regarding enclosure and warning signals. The custom operating software was coded, tested, and fully debugged, the instrument was evaluated, and ion filtering was demonstrated by scanning the FAIMS stage and monitoring the IMS detector signal. Struggling to obtain the expected resolving power, we replaced the original homemade Tyndall gate with a commercial product specifically for IMS use. Additionally, we installed some resistive heaters and thermocouples for temperature control.

During FY 2009, we completed assembly of a new FAIMS/IMS system operating at atmospheric pressure, with the IMS drift tube heated and ions pulsed in by a gate. These modifications to the initial design allowed us to produce high resolution two-dimensional FAIMS/IMS separations at ambient pressure. Initial tests were performed employing the ion source. For example, tetrabutyl ammonium bromide cations are transmitted by FAIMS and identified by mobility measured in IMS over a narrow range of compensation voltages near −5.3 V. At compensation voltages differing by 1 V or more (−4.5 V), there is no trace of tetrabutyl ammonium bromide, but two other ammonium bromides persist. The baseline width of 1 V for the transmission window is standard for (1+) ions such as tetrabutyl ammonium with the planar FAIMS used in this work and shows that high FAIMS resolution is retained in the present system. The resolving power (R) of drift tube IMS in these spectra is approximately 80, which compares to or exceeds performance of commercial IMS systems at over 70 percent of the theoretical limit based on the drift voltage. In atmospheric pressure IMS, achieving nearly 75 percent of the theoretically maximum R is standard, demonstrating that the IMS stage of present system operates as well as commercial IMS analyzers. These results meet the minimal stated objectives of this effort.

However, we have faced real sensitivity problems: reliable detection required high sample concentrations, and the *s*/*n* ratios were often low. This is partly due to limited ion transmission efficiency of the planar FAIMS device used caused by a sub optimum circular aperture in front. Implementation of slit aperture interfaces, with a contiguous slit or linear array of circular apertures, at the entrance (and exit) of planar FAIMS analyzers has improved sensitivity of FAIMS/MS platforms by order of magnitude. Using a slit shaped multihole aperture at the FAIMS entrance (in conjunction with multi emitter electrospray ionization) has increased sensitivity to enable detection of RDX explosive where none could be seen above noise otherwise. However, sensitivity still did not suffice for practical analyses, apparently because of poor ion transmission through the FAIMS/IMS interface. Further optimization of this new interface is needed to make good use of the resolution advances made in this work.



CV/DV map for DNT vapors in the anion mode obtained using FAIMS microchips.

With Owlstone Ltd., we jointly developed FAIMS microchips, a new format where ions are filtered in about 30 μs, which is nearly 100 times faster than in previous FAIMS systems. This speed allows rapid acquisition not of just FAIMS spectra but of whole compensation voltage/dispersion voltage maps that aggregate those spectra over a broad range of FAIMS dispersion voltages. Such maps enable more specific and reliable identification of explosives, as shown for the DNT vapors in the figure. We recently coupled these microchips to mass spectrometry. Considering the high transmission efficiency of these FAIMS chips, coupling them to IMS is one approach to more sensitive FAIMS/IMS analyses.

Standoff Concealed-Device Detection and Signature Analysis using Non-Imaging Sub-Millimeter Wave Radar

David M. Sheen

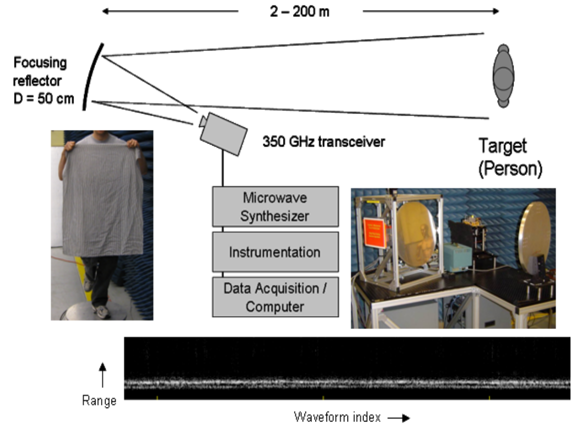
◆ Standoff detection of suicide bombers or personnel carrying other concealed weaponry is of fundamental importance for homeland security and military force protection. ◆

Millimeter wave imaging techniques have been well-developed for the detection of suicide bombers and other concealed weapon threats within security screening portals. However, systems that can operate effectively at significant standoff ranges (up to 100 m) do not yet exist. At these ranges, the resolution achievable by millimeter wave and submillimeter wave systems is limited, and it may not be sufficient to detect and identify concealed explosives. This project's objective is to develop submillimeter wave radar technology that detects concealed objects using non imaging signatures. These may include detecting target depth variations, polarization signatures, and scattered intensity abnormalities. The primary challenges for standoff detection of concealed weapons are due to the uncontrolled nature of people's movements, sensitive detection at extended ranges, clothing penetration, and variable returns from the radar system. Submillimeter wave radar technology is promising for this application because it has been demonstrated to penetrate clothing effectively, reflect from concealed objects, and can propagate over hundreds of meters without excessive losses.

A frequency range centered near 350 GHz was chosen for this application by considering the tradeoff between atmospheric transmission, excessive diffraction (beam width control), and clothing penetration. A complete radar system was designed and assembled (block diagram and photograph in the figure). Initial measurements were conducted using a small retro reflector and human subjects up to 50 m, a distance at which the system shows excellent sensitivity. The system was improved dramatically with a new transceiver architecture that uses a high-speed arbitrary waveform generator. It can acquire thousands of waveforms/sec, up from 5 waveforms/sec with the previous system. A parabolic collimating reflector was designed and fabricated to eliminate optical aberration in the previous spherical mirror.

Using this system, a number of experimental time history measurements were collected from a human subject at 10 m with and without a concealed mock explosive belt. For each measurement, the subject was directed to stand still, walk in place, or rotate 180 degrees. The data normally collected by the radar system are in phase waveforms over a 345.2 to 354.8 GHz (9.6 GHz bandwidth) frequency sweep at a repetition rate of several hundred waveforms/sec for a time history of approximately 10 sec. These data were processed by first performing a phase calibration to sharpen the range resolution to near theoretical limits and then performing a fast Fourier transform on each waveform to display a high resolution range profile of the returns. The system configuration and an example result are shown (bottom of figure), which are radar returns for a person walking in place in the radar system beam with a concealed mock explosive behind a piece of cloth. The range profile clearly indicated the reflection in front of the return from the explosive and the man's body.

Initial observations of clothing with this system indicate that clothing reflections are significant, so experiments were conducted to quantify the effects of clothing reflection of various types and configurations. Orthogonal polarization experiments were conducted; however, initial results indicated no significant reduction in clothing reflection relative to target response. Range resolution of the system has the potential to isolate clothing, explosive, and body reflections. System range resolution was doubled by modifying the transceiver for twice the bandwidth, and experiments confirmed the increase in range resolution.



Experimental system configuration (top), photograph of experimental sub-millimeter radar system (right), imaging test subject (left), and 350 GHz radar range time history data for a person walking in place with a concealed mock explosive (bottom).

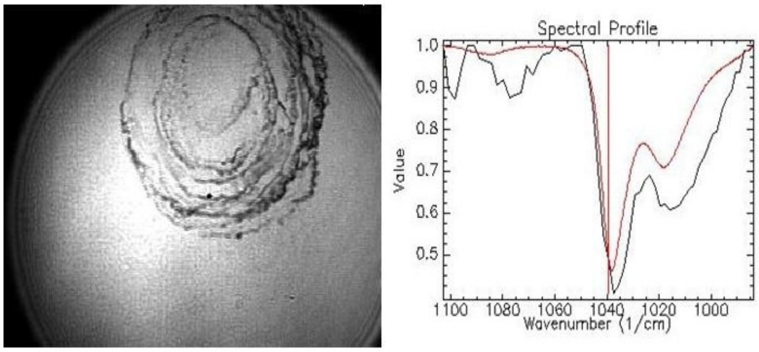
Substantial progress was made on this standoff detection project in FY 2009. The radar system was improved through the design and implementation of higher performance optics, orthogonal polarization, and a faster transceiver with increased range resolution (bandwidth). Experiments verified improved performance, but clothing reflection remains a significant barrier to implementation of this technique. Imaging may be required to isolate clothing reflection, concealed explosives, and the human body.

Standoff Hyperspectral Imaging of Explosives Residues Using Broadly Tunable External Quantum Cascade Laser Illumination

Bruce E. Bernacki, Mark C. Phillips

◆ Standoff detection of explosives residue is essential to meet homeland security threats and to assess and improve military force protection. Active hyperspectral imaging will provide rapid, unambiguous spectral identification of suspicious substances combined with image contextual clues for rapid identification and classification of explosive residues without the need for sample preparation or physical contact. ◆

Rapid identification of explosive threats is an ongoing need for homeland security and force protection. Prior research shows that it is feasible to detect approximately 100 µg quantities of explosives on surfaces using ratio images of explosives residue illuminated by infrared lasers tuned to on and off absorption features of the explosives. However, the sparse dataset that resulted made reliable detection challenging. By using a continuously tunable mid-infrared illumination source (such as an external cavity quantum cascade laser), one can probe the detailed absorption features of unknown samples that lie within the tuning range of the laser. An image hypercube is formed by recording representations at each tuning step of the external cavity quantum cascade laser. The resulting images can then be exploited using hyperspectral image analysis methods developed by the remote sensing community for spectroscopic material identification. At the completion of this project, we will demonstrate near-field and standoff detection of explosives residue at 10 m or greater.



Near field images show RDX on an aluminum plate with 100 µg/cm² areal density. The image of the RDX under the external cavity quantum cascade laser illumination is seen at left. The spectrum recovered from one pixel in the image is shown at right (darker color trace) along with the reference library spectrum (lighter trace).

In FY 2009, we constructed the experimental setup and obtained data at near field and modest standoff distances. The basic system consists of the external cavity quantum cascade laser, LabVIEW control software (used to synchronize the laser scan and the image capture to form the image hypercube), control computer, and microbolometer camera. The illumination source is a custom built external cavity quantum cascade laser operating in a quasi continuous wave mode with a 100 kHz modulation rate and swept across a tuning range from 983.8 to 1102.95 cm^{-1} (9.07 to 10.16 µm) in 2 seconds with 2 cm^{-1} resolution. The resulting hyperspectral image has 60 wavelength bands, which is adequate to identify the broad spectral features that are characteristic of explosives.

Initial work began by working in a transmission setup in order to test the hardware and software functionality. Tetryl was deposited on a BaF_2 window to obtain an areal density of 20 µg/cm^2 and imaged at a distance of 100 mm. The spectrum of pixels within the image showed good agreement with the library spectrum for Tetryl. The near-field setup was changed to reflection mode imaging using a sample of RDX on an aluminum substrate with an areal density of 100 µg/cm^2. The hyperspectral image showed close agreement with the library spectrum for RDX. Additional algorithms were employed to identify the residue to include a least squares spectral fitting algorithm and matched filter approach in which the unknown spectral features at each pixel are compared with library spectra. Principal components analysis was also employed as an anomaly detector to highlight the presence of unknown substances. Finally, standoff imaging was demonstrated by moving the RDX sample to 4.2 m and was positively identified using the least squares spectral feature fitting to show the location and relative concentration of RDX.

In summary, we constructed a basic experimental setup (including an external cavity quantum cascade laser), control computer, software, and imaging camera, and obtained proof of concept data in which RDX with an areal density of 100 µg/cm^2 was positively identified using active hyperspectral imaging with external cavity quantum cascade laser illumination at a standoff distance of 4.2 m. During FY 2010, we will extend the standoff distance greater than 10 m and expand the explosives sample list to include RDX, TNT, and Tetryl. This will require closer attention to illumination and imaging optics to obtain the necessary resolution for positive identification and reduce image artifacts due to coherent illumination.

Standoff Infrared Detection of Explosives

Thomas A. Blake, James F. Kelly, Timothy J. Johnson

◆ The objective of this project is to develop advanced methods of spectral and spatial information mapping or filtering that can be used with the emerging commercial hyperspectral imaging (HIS) systems to enhance port and infrastructure security. ◆

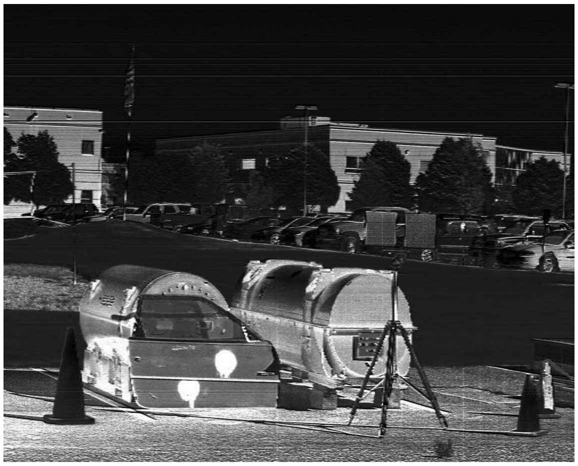
Stand-off detection of explosive residues left as first or second generation fingerprints can provide fast analysis of suspect containers and vehicles while working at a safe distance (greater than 50 to 100 m). Laser based concepts are potentially feasible, but the best (such as laser induced breakdown spectroscopy) require high laser power and can readily damage eyes or surfaces to achieve requisite sensitivities. This project will build on prior research successes using a single element Fourier transform infrared spectrometer (FTS) to detect deposits of low-volatility chemicals with areal dosages. With the appropriate field measurements on a variety of surfaces over a range of concentrations, we will rapidly determine the feasibility of using this type of technology for detecting explosive residues.

During FY 2008, infrared reflection spectroscopy data was collected from explosive residues on various surfaces using a single pixel and an imaging FTS (7.7–12.5 µm). Illumination of the surfaces was done either actively using an infrared lamp or done passively using cold sky shine. A subset of the imaging data was analyzed and published in FY 2009 as an invited article in a special issue on explosives detection in *Analytical and Bioanalytical Chemistry*. The published work used anomaly and target detection statistical algorithms to analyze infrared images of three bare metal plates each with a small central stain of RDX. Data analysis detected and classified even the lowest dosage stain at the greatest distance. The paper also includes a detailed discussion of how improvements in detectivity can be made in infrared imaging detection.

Another data set recorded in FY 2008 using the imaging FTS included solid chemical compounds (sodium chlorate and ammonium nitrate) spread on and under soils. We were able to produce infrared spectroscopic images of these compounds even when buried under 3 mm of soil. As with the previous data set, the scene, a tray of soil with the chemicals either on top or buried under the soil, was illuminated passively with cold sky shine. We were able to replicate these experiments in the laboratory in FY 2009 using a benchtop FTS. These experiments also showed that *p*-polarized light can preferentially penetrate soils compared to *s*-polarized light. These results may indicate subsurface chemical detection. A manuscript describing these results has been prepared and submitted in October 2009 to *Applied Optics*. Other data sets associated with the FY 2008 field collection are being analyzed, including active and passive detection of explosive residues on bare and painted metal plates and a car door.

While working on the infrared imaging experiments, we noticed that the nitramine compounds TNT and tetryl turned brown and yellow, respectively, when exposed to sunlight. This presented us with the idea that we could detect and identify these compounds colorimetrically on painted surfaces, providing us with complimentary signatures to the infrared. During FY 2009, we prepared a number of bare and painted metal plates with explosive residues (TNT and RDX) and used a visible and near infrared laboratory imaging spectrometer to record spatially resolved spectra of the stains on these plates, which were illuminated with ultraviolet or visible light. We discovered that TNT has a broadband spectroscopic signature in the visible when illuminated by a halogen lamp. Further experimentation will be required to determine if this visible signature is unique. More interestingly, RDX preferentially scatters 365 nm light from an ultraviolet blacklight. We have since taken the imaging spectrometer outside and are recording sunlight illuminated images of the car door.

Continuing the visible imaging spectroscopy experiments will be part of FY 2010's work. We still have a considerable backlog of infrared images recorded during FY 2008 that need to be analyzed and reported. Based on these results, we have developed new ideas on how best to use the Telops infrared imager.



Visible spectral fitting of the TNT (upper right) and tetryl (lower middle) stains on a car door. The TNT stain areal dosage is 42 $\mu g/cm^2$, and the tetryl stain is 37 $\mu g/cm^2$. Viewing distance is 14 m, and illumination is by sunlight.

Standoff Radiography

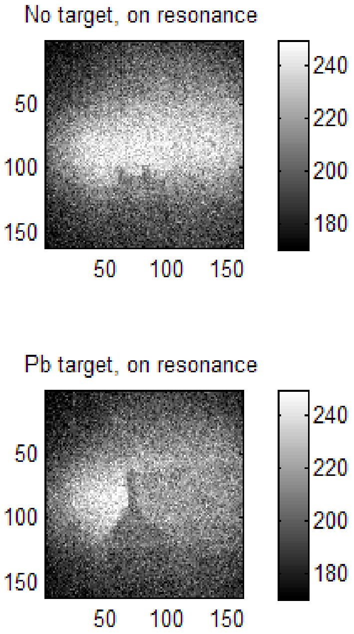
David V. Jordan, Warren W. Harper, Glen A. Warren, Albert Mendoza, Patrick N. Peplowski

◆ This project investigated the feasibility of performing standoff transmission radiography by measuring the air fluorescence ("air glow") signature of ionizing radiation fields generated by active interrogation of material samples with a photon beam. Successful application would permit collection of useful radiographic data relevant to proliferation detection at standoff distances substantially larger than currently possible with conventional transmission radiography. ◆

Standoff detection of special nuclear materials is a key mission goal of current proliferation detection research and development. Many approaches to standoff detection focus on "direct" detection of gamma-rays or neutrons produced by radioisotope decay or beam reactions. Attenuation in air typically limits these direct techniques to distances under 100 m. Alternatively, detecting a "secondary" signature of ionizing radiation in air via nitrogen fluorescence offers the potential for long-range (100 m to 1 km) measurement of the energy deposition rate of radiation fields.

The current project exploited the air glow signature in the development of a novel technique that combines elements of traditional radiography (i.e., interrogating a sample with a penetrating, high-energy photon beam) with standoff visualization of the spatial pattern of radiation dose rate in air near the sample. In tandem with an appropriately portable and field deployable accelerator technology, existing optical imaging techniques support sensitive detection of the air glow signature that could readily distinguish light from heavy containerized materials in a variety of inspection scenarios. The method may ultimately provide a tool for identifying the characteristic spatial patterns of penetrating ionizing radiation products emitted from shielded fissile materials bombarded by an interrogating photon beam.

The research involved collecting radiographic images with an optical imaging sensor (charge coupled device based telescope) viewing sample targets exposed to high energy (5 to 10 MeV) bremsstrahlung photon and electron beams. We performed experiments at the Idaho Accelerator Center over a relatively short (3 m sensor-to-target) standoff distance in these proof-of-concept experiments. The beam impinged on a variety of slab-shaped targets (graphite, aluminum, steel, lead, and depleted uranium), each available in several thicknesses (typically 0.5 to 3 in). The sensor viewed the target "side on" with a field of view of approximately 70 cm. In this geometry, the sensor registered the air glow pattern both upstream and downstream of the target in a single image. The main quantity extracted from the images is the ratio of optical signal rates from two sides of the target, *R*. In a naïve physical model, beam attenuation in the target should result in a less intense beam down-stream, yielding a smaller air glow signal. (Additional effects such as backscatter and emission of secondary particles from the target can complicate this simple model.)



Air glow pattern recorded over 70×70 cm^2 field of view with a 10 MeV electron beam traversing images from left to right. Upper image, no target; lower, 2-inch lead target.

The experimental results for all the materials tested show a statistically significant dependence of the ratio *R* on the target thickness. This dependence is in qualitative agreement with the expectation that a thicker target should cause greater attenuation. Monte Carlo simulations of the coupled (radiation transport + air glow generation + optical detection) processes generally reproduce the average measured air glow intensity to within a factor of two. However, simulations do not reproduce the spatial pattern of the air glow data in detail, and in general over predict the contribution to *R* of simple beam attenuation by about three. Relatively large ultraviolet backgrounds, evidently produced by non-nitrogen fluorescence of bulk materials (such as the beam dump) in the experimental hall, complicate comparison of simulation to data.

These experiments constitute a first of a kind demonstration of the radiographic technique. The results strongly suggest that material thickness information can be measured at standoff by an appropriate application of the method. Data do not demonstrate that discrimination of special nuclear materials from various heavy materials of high atomic number (e.g., lead) is possible with this technique. However, definitive evaluation will require outdoor field testing, where optical background rates from beam interactions with proximate bulk materials are expected to be substantially lower than those in the experimental hall.

Understanding Ice Formation in the Atmosphere

Daniel J. Cziczo, Gourihar R. Kulkarni, Mikhail S. Pekour

◆ According to the most recent Intergovernmental Panel on Climate Change report, the single most uncertain aspect of climate change is the interaction of small atmospheric particles and clouds. While there are several mechanisms by which clouds form, the formation of ice crystals is the most uncertain and is the specific focus of this project. ◆

Carbon dioxide is understood to be the most important of the greenhouse gases in terms of impact on climate change because of both its anthropogenic origin and large radiative forcing. What is not clearly communicated is that the climatic impact of carbon dioxide is resolved, though both its abundance and impact are understood with higher certainty. Other climatic factors are not as well realized, and it is these unknowns that determine our current inability to predict future climate accurately. The most important of these are small particles known as aerosols.

By themselves, aerosol particles can affect the earth's climatic balance by absorbing or scattering solar and terrestrial radiation, which is a process known as the "direct effect." It has been understood for several decades that small atmospheric particles can initiate the formation of clouds by creating liquid water droplets or ice crystals. Clouds also play a role in global climate either by trapping terrestrial radiation or reflecting solar radiation back into space. The sign of this forcing – net warming or cooling – is dependent on the altitude, location, persistence, and the thickness of the clouds. Because aerosols affect these specific properties, this is known as the particles' "indirect effect" on climate.

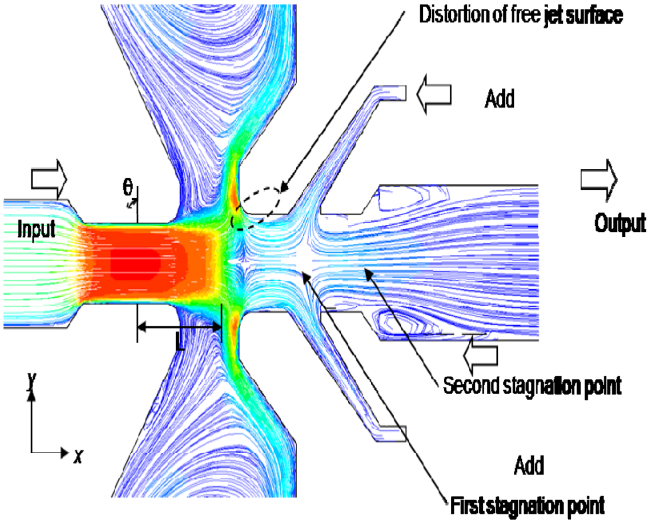
The formation of liquid water clouds has been extensively studied. The indirect effect is typically sub-divided into explicit ways in which aerosols affect clouds, and the first and second indirect effects are generally considered to be formed purely due to warm clouds. The impacts of pure ice as well as clouds that have both liquid and ice (known as "mixed-phase" clouds) are not well known because they are typically at increased altitude or high latitude location, which has made the field study of ice and mixed-phase clouds much more challenging. Likewise, laboratory studies of ice and mixed-phase clouds are more difficult due to a requirement of high precisions measurements at low temperatures and water vapor levels. The climatic impact due to ice crystals is the "glaciation effect" portion of the indirect effect and, for the aforementioned reasons, it too remains ill-defined.

It is also significant to note that there are important reasons to study atmospheric ice nucleation beyond climatic uncertainty. For example, ice nucleation is a critical element of the global water cycle. Indeed, the majority of terrestrial precipitation is believed to be initiated by ice nucleation. With this in mind, the foremost objective of this project is to understand which aerosol particles initiate atmospheric ice formation so that we are better able to reduce the uncertainties of climate change and more thoroughly understand the global water cycle. Among the specific foci for our studies are three determinations: 1) the exact conditions (relative humidity and temperature) required for ice formation, 2) the effect that anthropogenic activities (specific components such as combustion by-products as well as secondary surface coatings of sulfate and organics) have on ice formation, and 3) the interrelationship of droplet and ice formation (i.e., which aerosol particles form drops and which form ice).

First and foremost, the objectives of our project are being met by the development of two novel instruments. The first is a compact ice chamber that can mimic the formation of ice clouds. This is of extreme importance because it means that researchers need not travel to locations where atmospheric ice formation takes place nor must they go during the precise moment that it is occurring. Instead, the chamber allows researchers to make artificial ice clouds in the laboratory from specific chosen particles, or there is the option to travel to locations where ice clouds form without having to conduct experimentation only at those times when nucleation happens to take place. Examples include laboratory experiments on aerosols that mimic combustion products such as soot and field studies at high altitude sites or from aircraft.

Three-dimensional simulation of the compact ice chamber.

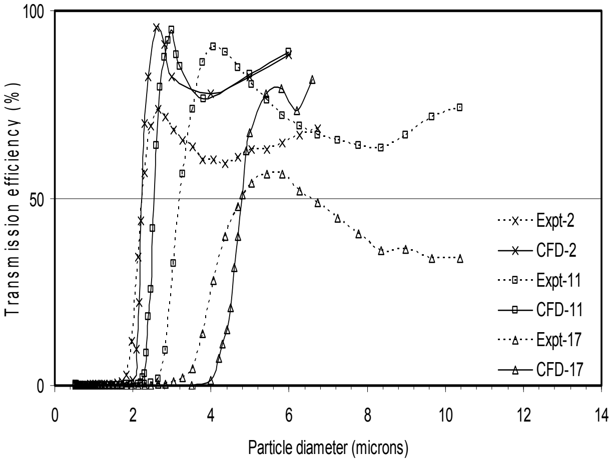
The compact ice chamber was completed in FY 2009 and has undergone laboratory testing. The initial deployment of the chamber will take place in January 2010 at the Desert Research Institute's Storm Peak Laboratory located at approximately 10,000 feet above sea level in Colorado's Rocky Mountains. This site offers access to particles that form ice clouds without the expense and constraints of a research aircraft, making it an ideal location. Depending on the meteorological conditions, we anticipate a 4- to 6-week field study. The data produced at this study should form the basis for several peer-reviewed scientific papers. Storm Peak will also be the location of the DOE ARM Mobile Facility 2 during 2010–2011. The chamber has been funded by DOE to return to Storm Peak and conduct research in concert with the ARM Mobile Facility instruments.



Computational fluid dynamic simulation of the flow through a counterflow virtual impactor.

The second novel instrument system known as an advanced counterflow virtual impactor, which separates either ice crystals or droplets from the other and from unactivated aerosol particles, is being developed (see the figure above). A conventional virtual impactor was completed in FY 2009 that separates large particles from small and thus can be used to differentiate ice crystals from unactivated aerosols. Extensive computational fluid dynamic modeling has for the first time been compared to laboratory experiments as part of this project. Additionally, this unique research forms the basis of a currently submitted peer-reviewed publication to *Aerosol Science and Technology*. The conventional impactor is being coupled with the compact ice chamber for the upcoming field deployment, which allows the separation and analysis of those particles that nucleate ice as a function of relative humidity and temperatures using techniques such as single-particle mass spectrometry and electron microscopy. Our expertise with computation fluid dynamic modeling and the conventional impactor has allowed us to begin construction of the more complex advanced counterflow virtual impactor, which will also separate by phase. This system will be used for laboratory studies during summer 2010, and we anticipate field deployment later that year.

FY 2008 represented the first year of this effort, with our work focused on instrumentation design. Staff required to undertake this project were identified, including an expert in ice nucleation. Dr. Gourihar Kulkarni built our capability to design and computationally test apparatuses such as the compact ice chamber, conventional impactor, and advanced counterflow virtual impactor before actual fabrication. This ability to model instrument performance prior to fabrication and experimentation forms the basis for the aforementioned impactor publication. Additionally, wet chemistry and instrumentation laboratories became operational in August 2008 in the Atmospheric Measurement Laboratory, a facility that previously did not have this capability. A general set of aerosol production and characterization instruments, a prerequisite for the advanced studies that have been conducted in this project, was also obtained. These included apparatuses to produce dry and wet particles and to characterize their size, phase, and chemical composition.



Comparison of computational fluid dynamic model with experimental results for a conventional counterflow virtual impactor.

During FY 2009, we focused on the fabrication, integration, and testing of instrumentation. The compact ice chamber was constructed, flow testing performed, the chamber mated to the refrigeration system, and the control software finalized. The ice chamber is currently in a configuration for the field studies that will take place at Storm Peak. The conventional counterflow virtual impactor has been experimentally tested for use in field and laboratory settings, and the results have been compared to our fluid dynamics model. The impactor is currently being coupled to the compact ice chamber for the field study.

Also during FY 2009, our team also undertook a joint venture with ETH-Zürich (the Swiss Federal Institute of Technology) to study mineral dust's hygroscopic properties of mineral dust. Mineral dust is a known ice nucleus, but the drop formation potential in mixed-phase and warm clouds was not previously well known. The results were of significant importance, enough to be invited for publication in *Physical Chemistry Chemical Physics*. A second joint study with the University of California-San Diego concentrated on the design of a Humidified Tandem Differential Mobility Analyzer coupled with the virtual impactor for use with a warm cloud chamber. This configuration will offer the unique opportunity to complement our ability to ascertain which particles form ice crystals with the additional benefit of determining which particles form droplets. Thus, we will be able to perform experiments on both of the phases present in the climatically important "mixed-phase cloud" regime.

In addition to instrument development and laboratory activities, all members of the ice nucleation group worked on pre-existing data sets during FY 2009. Resulting from our studies and research, a total of six peer-reviewed journal articles on drop formation and ice nucleation were published, three more are currently under review, and two others are in preparation. Other 2009 efforts of particular note included the following:

- The importance of hygroscopicity and droplet formation found during our collaboration with ETH encouraged us to revisit a data set obtained in the Arctic using single-particle mass spectrometry. Analysis of these data has led to three publications that appeared in *Journal of Geophysical Research – Atmospheres*.
- Drs. Kulkarni and Cziczo have revisited several other data sets on ice formation while constructing the compact ice chamber and virtual impactor. One of these concerns, the climatic importance of anthropogenic lead due to ice formation, appeared in *Nature Geosciences* in May.

Laboratory studies will also take place throughout FY 2010. In January, the chamber/virtual impactor combination will be field tested, and final construction and validation of the advanced counterflow virtual impactor will take place during spring and summer. We anticipate data reduction and publication production from the results obtained at Storm Peak will take place during this time period as well. We anticipate an additional four peer reviewed publications as a result of these laboratory and field studies.

Biological Sciences

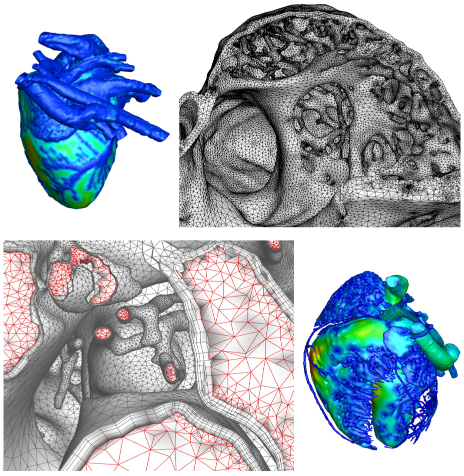
A Geometric Framework for Multimodal Analysis of Cardiac Tissue Using Magnetic Resonance Imaging, Histopathology, and Proteomics for the Identification of Biomarkers

James P. Carson, Sam J. Harbo, Kevin R. Minard

◆ Through joining biomedical data from different sources, this project aims to facilitate the prediction and understanding of biological pathways for environmental response and heart disease to enable early detection, intervention, and amelioration of heart health challenges. ◆

Understanding mortality and morbidity associated with the heart is paramount to improving human health. Increasing amounts of evidence are emerging that link natural and manmade environmental factors to cardiac diseases and often fatal decreases in heart muscle performance. In support of efforts to address this challenge, we developed a computational geometric three-dimensional model of the mouse heart that will facilitate predicting and understanding the biological pathways of environmental response and heart disease. The future integration of different types of data modalities including proteins, pathology, and magnetic resonance imaging offers an opportunity to link noninvasive imaging with biomolecular profiling, thus enabling a novel approach for the early detection, intervention, and amelioration of heart health challenges.

With the advent of proteomic data collection capabilities, a growing, unmet challenge is the development of computational technology to support the analysis, visualization, and distribution of proteomic data and their comparison with other data modalities. This challenge is compounded when one adds a spatial component to the data, which may be in two or three dimensions. Past efforts at identifying biomarkers and pathways in the heart have either utilized low-resolution whole-heart methods that lack spatial information or focused on specific quantities of isolated information. Critically important to overcoming limitations of current experimental methods is the capability to organize high-resolution data accurately and reliably for the entire heart.



Three-dimensional multi-material heart model, including tissue (top) and fluid (bottom).

This project addressed the challenge in part by constructing a multi-material geometry of the heart suitable for simulations and in association with different data modalities, from proteins to pathology to MRI. Using this heart framework, we developed the ability to produce multi-modal digital image volumes of the mouse heart by co-registering and aligning data obtained from MRI, histopathology staining, and proteomic profiling. This framework creates the capability to facilitate the discovery of biomarkers through rapid integration of such datasets. We accomplished these objectives through a new method for collecting MRI data by synchronizing the image collection with the heart beat, thus increasing the resolution. To gather biomolecular response data, we developed methods to examine thinly sliced frozen tissue sections of mouse heart using matrix-assisted laser desorption/ionization to profile protein abundance. We also performed studies to examine protein perturbations within the heart by injecting mice with nanoparticles and characterizing the extent of nanoparticle deposition with protein regulation. To link these data from different modalities (MRI and proteomics), two-dimensional atlases of mouse heart tissue slices were created using a subdivision-based deformable grid platform to represent the heart anatomy at multiple resolutions. In addition, a three-dimensional representation of the mouse heart was created. This model of the heart represents both the heart tissue and the vasculature fluids at high detail. Anatomical features of the heart model include valves, chordae, and coronary vasculature. This three-dimensional heart allows comparisons of normal heart function with abnormal function as well as the identification of regional expression profiles that correlate with heart disease.

Ultimately, the geometric framework developed for multimodal analysis of heart tissue will be applicable to localize heart disease factors rapidly and enable discovery of disease phenotypes biomarkers. For example, congestive heart failure is an incurable condition that affects over 5 million Americans. Developing techniques for early detection and understanding the etiology for this disease are critical steps toward reducing or even eliminating this threat to human health. The combination of causes of heart failure and associated acute events is poorly understood. The integrated modeling of magnetic resonance imaging, histopathology, and proteomics will be powerful in delineating specific mechanisms. Further, the model can eventually be used to monitor and interpret environmental factors (e.g., particulates, chemicals, etc.) or drug therapeutics in real time relative to a standard atlas of the heart.

A Multidisciplinary Approach to Engineer Xylose and Arabinose Utilization for Ethanol Production by Saccharomyces cerevisiae

Ellen A. Panisko, Scott E. Baker, Heather A. Colburn, James R. Collett, David S. Wunschel

◆ We are using a systems science approach to gain an understanding of how carbon in the form of simple 5 and 6 carbon sugars is utilized for growth and fermented into ethanol by *Saccharomyces cerevisiae*, brewers' yeast. Our goal is to use that knowledge to engineer strains with increased efficiency for fermentation of xylose and arabinose into ethanol and apply the information gained to other fermentive organisms. ◆

The current rise in energy costs due to the increasing price of petroleum has moved biofuels, such as ethanol, into the United States collective consciousness. A large percentage of the ethanol produced in the country is made by fermentation of glucose (derived from corn starch) to ethanol using *S. cerevisiae*. However, for ethanol to become and economically viable alternative to petroleum based fuels, a number of technical bottlenecks will have to be overcome. To meet these needs the ethanol industry must move beyond corn starch as the biomass source for fuel production. More complex plant biomass which has cell walls composed predominately of cellulose and hemicellulose will need to be utilized as the carbon source to produce glucose and pentose sugars for fermentation to ethanol. *S. cerevisiae* is unable to use the major pentose sugars that constitute hemicellulose, xylose, and arabinose. We will use genetics, metabolomics, and computational modeling to generate the data necessary for engineering of *S. cerevisiae* into an organism with efficient pentose use for ethanol production.

The purpose of this project is to gain familiarity with approaches for metabolic engineering of yeast for pentose use and ethanol production. The three main approaches we are using (genetic analysis and manipulation, metabolomics, and computational modeling) are interdependent in that data generated by one approach can be fed into the other two approaches. For example, metabolic and growth (i.e., biomass) information is fed into the computational model to improve its predictive ability. Detection of metabolic bottlenecks can indicate the need for higher (or lower) expression of a given gene product. We are taking a forward and reverse (directed or nonrandom) approach to genetic analysis and manipulation. The mutant strains generated can be used to validate or refute a computational model prediction and are used to generate samples for metabolome and growth analysis.

During FY 2007, we established the computational modeling aspect for the project and conducted molecular genetics and carbohydrate analysis. A fully compartmentalized genome-scale metabolic model was selected as a base model to use in this research. The systems biology markup language was chosen to represent the metabolic reaction network model in a computer readable format. Several linear programming solvers were also selected to solve the optimization models for the work.

In FY 2008, two strategies were used to complete the cloning of the five genes to be introduced into *S. cerevisiae*. The first was to modify restriction site usage within the original cloning strategy; the second was to generate new parallel cloning in case of additional restriction site problems. All primers were ordered and received, and over 95 percent of polymerase chain reactions for the parallel strategies were completed. The goal was to alter the model to introduce genes responsible for xylose and arabinose catabolism into the yeast and observe effects on the metabolic model.

After problems with an unexpected restriction site introduced (the deoxyribonucleic acid sequence was not identical to that published for *S. bayanus*) into one of the promoters to be used for expression of genes from *Aspergillus niger* that metabolize xylose and arabinose during FY 2008, a modified cloning strategy was undertaken in FY 2009. All polymerase chain reactions for the parallel strategy were completed. Final steps in vector construction were undertaken in concert with performing DNA sequencing to verify that no errors were introduced by the polymerase chain reaction technique. Two genes amplified from *A. nige*r for xylose and arabinose utilization were identified to have missense mutations, and a pathway to correct these mutations was designed for a follow on project.

The computational modeling effort utilizes a yeast metabolic model named iND750, which includes 750 genes and over 1100 metabolic reactions. The model was altered to introduce the five genes that are responsible for xylose and arabinose catabolism in *A. niger* into the yeast model. This project was successful in establishing a metabolic modeling capability within our group and provided the basis for an additional research project.

The final carbohydrate analysis method was defined and validated. The protocol is a three-day procedure followed by gas chromatography coupled to time of flight mass spectrometry. Results indicated this procedure to be robust with respect to reproducibility for sample and biological replicates. This procedure will be utilized in follow on projects that examine sugar utilization by fermentive organisms.

Analysis of Functional Diversity in Microbial Communities for Organic Carbon Transformations

Allan E. Konopka, Vanessa L. Bailey

◆ The increase in carbon dioxide fluxes to the atmosphere has raised global concerns regarding climate change. Carbon sequestration is one strategy being developed to mitigate carbon dioxide emissions. This project is focused on the activities of soil microbes that can lead to the formation of recalcitrant plant derived organic carbon that will remain sequestered in soil. ◆

A critical component in biofuels and carbon sequestration is the functional diversity of microbial communities. Although molecular methods such as analysis of ribosomal ribonucleic acid gene sequences have provided insight into the memberships of microbial ecosystems, significant technology development remains to produce adequate methods to monitor their activities. Robust methods to analyze microbial functional diversity are a topic of current research. A variety of molecular based tools have been used, including specific probes and polymerase chain reaction primers and metagenomic analyses. In this project, we aim to develop the analysis of soil microbial composition via targeted sequencing of the community metagenome and analysis of functional activity at the scale of a fundamental particle in soil, an individual soil aggregate. We will develop novel methods to couple activity measurements to phylogenetically informative biomolecules by the application of stable isotope probing by using stable C and water isotopes that have the advantage of not acting as a selective force on microbial community composition.

Our research focused on two goals. The first was to analyze the targeted sequencing obtained from the metagenomes of individual soil aggregates to further our understanding of the prokaryotic community structure and its variability between individual aggregates. The second objective was to scale down the analysis of total microbial activity to permit measurement of these microbial community properties in individual soil aggregates. We also carried out statistical analysis of variability in activity and resiliency to environmental perturbations.

Interpretation of Large-Scale Sequence Information Gathered Through Pyrosequencing. The microbial community was very diverse in individual soil aggregates and was dominated by actinobacteria (25 percent of total sequences), bacteroidetes (23 percent), acidobacteria (9 percent), and alpha and beta proteobacteria (25 percent). Within these clades, the operational taxonomic units (defined as sequences that are greater than 97 percent similar) differed substantially among individual soil aggregates. Focusing on a single representative clade, the actinobacteria, diversity falls off more sharply for individual aggregates than for whole soil or pools of aggregates. This, however, may be an artifact of the disparity in the number of sequences reported for individual aggregates and pools; the number of sequences was smaller (1000-3000 compared with 30000-60000) for the individual aggregates.

A few lineages were detected in high relative abundance in multiple samples. These include six operational taxonomic units within acidobacteria-4, and operational taxonomic units in the bradyrhizobiales, saprospirales, moraxellaceae, and propionibacteriaceae. The phylogenetic diversity within individual aggregates was much smaller than found in bulk soil. Where we estimated that bulk soil contained 4800 distinct operational taxonomic units, individual aggregates contained less than 300. However, because few operational taxonomic units were shared among individual aggregates, one can see why a very high level of diversity is found when bulk soil is analyzed.

Scale-Down of Physiological Assays of Community Biomass and Functionality. The microscale analysis of individual aggregate function and biomass was developed using a methylumbelliferyl based assay of β-glucosidase (functionality), followed by measurement of total adenosine triphosphate (active microbial biomass) in the retained soil pellet. This was found to be a harmonious pairing, as a certain amount of adenosine triphosphate is lost during the enzyme assay; however, this seems a relatively constant proportion (approximately 33 percent) of the total adenosine triphosphate in aggregate. Using these techniques, we measured enzyme activity within sub mg masses of individual soil aggregates in 1 to 2 hour incubation time. These analyses suggest very significant differences in activity among individual small aggregates (250-425 µm diameter) but smaller activity differences in aggregates with diameters of 425-841 and 841-1000 µm.

Approaches in molecular and physiological ecology were scaled to a basic level at which interactions between physical, chemical, and biological components occur at the sub-millimeter scale. This work provided insights into fundamental biological ecosystem properties such as diversity. Similarly, experiments on microbial activity at this scale identified spatial heterogeneities in activity and resiliency taken into account in developing a predictive understanding of the role of microbial communities in carbon cycling. Important future factors to optimize are the enrichment of heavy isotope and the time period of labeling.

Application of a Systems Biology Approach to Understanding Protein Function

Karin D. Rodland, Harish Shankaran, Paul D. Ellis, David L. Stenoien, Chenghong Lei

◆ This project is directed at using a new approach of systems biology to understand protein function using a variety of model systems. In addition to furthering the Laboratory's capabilities in systems biology, we will be exploring applications that are relevant to human health. ◆

The genomics revolution of the twentieth century provided a "parts list" for living organisms ranging from microbes of bioremediation to humans. Yet, we still do not comprehend fully how these parts work together to define organism function. We have a vision that includes international recognition by providing the scientific leadership and technology needed to achieve a predictive understanding of multicellular biological systems from microbial communities to humans (i.e., microbes to man). The motivation for this program is the increasing need for a quantitative understanding of how cells interact with each other and their environment. We will push the state of the science in biology from a descriptive to a predictive science that will allow us to predict, manipulate, and potentially design multicellular systems and bioinspired solutions for bioenergy, contaminant fate and transport, carbon sequestration and global climate change, and human health.

PNNL has already developed novel proteomic technologies. What is lacking is a predictive understanding of complex systems applied to increasingly complex problem sets and the development and refinement of those capabilities to deal with more complex biological problems. The objective of this project is to facilitate the application of capabilities in mass spectrometry, magnetic resonance spectroscopy, systems biology, and bioinformatics to selected problems that represent high impact challenges in predictive understanding. We are applying proteomic and materials science capabilities to understand the relationship between protein structure, post translational modifications, and functional capability in complex cellular systems.

Described below is progress during FY 2009 that we made on the following research efforts.

Refine the Ability to Link Protein Structure With Function. The antiferromagnetic bis (μ-oxo) dimanganese(IV) complex $[Mn_2O_2(salpn)_2]$ was examined, with ^{55}Mn solid state nuclear magnetic resonance at cryogenic temperatures and molecular theory and values for the quadrupole coupling constant C_Q, and its asymmetry parameter η_Q. We observed a large anisotropic contribution to the shielding of each Mn^{4+} (i.e., a $\Delta\sigma$ of about 1300 ppm). Due to strong coupling within electrons manifested by this complex, more research is needed to explain molecular theory. Future efforts are required to explore more sophisticated computational methods for antiferromagnetic model compounds.

Determine the Stability and Activity of Complex Biological Molecules. Functionalized mesoporous silica particles were tested for their ability to bind and release antibodies (rat immunoglobulin G) for use as targeted therapeutics in cancer. Success was achieved in defining conditions for sustained release of immunoglobulin G from functionalized mesoporous silica particles under physiological conditions, and preliminary tests of efficacy against tumor xenografts in mice demonstrated significant anti tumor activity. These experiments established the proof-of-principle for using functionalized mesoporous silica particles in cancer therapy.

Apply Techniques to Understand the Systems Biology of Skin Response to Low Doses of Ionizing Radiation. Site directed mutations in mitotic and radiation sensitive serine 284 phosphorylation site on polo like kinase (PLK) 3 were made and inserted into green fluorescence protein vectors for localization experiments. Additional mutations at two sites to inactivate PLK3 activity were added to prevent problems with apoptosis induction. Gene expression studies demonstrated the importance of PLKs in response to variable radiation doses. An interesting dose dependent change in PLK expression was observed, where PLK1 is inhibited by low doses of ionizing radiation while PLKs 2 and 3 are induced by higher doses.

Validate a System Theoretic Model for Integrated Cell Signaling. Experimental data for the case of dual external stimuli were collected, and analysis indicated that we needed to include saturation effects in the transfer function model. With this change, the model captures all of our experimental observations. We demonstrated the correspondence between transfer function and traditional models based on ordinary differential equations. These results were used to refine the mechanistic model for ERK oscillations and to validate model predictions with targeted experiments, results of which have been submitted for publication.

During FY 2010, we will apply systems biology approaches to demonstrate the capabilities to predict the behavior of complex multicellular systems, predict effects of novel nanomaterials on biological systems, apply proteomic and systems approaches, and understand the effects of ionizing radiation on multicellular systems.

Community Diversity and Functional Redundancy of Cellulytic Microbial Communities in Soil Aggregates

Vanessa L. Bailey, Lee Ann McCue

◆ An understanding of the role of natural microbial communities in the global carbon cycle is fundamental to our ability to mitigate the effects of greenhouse gases. To gain this knowledge, we must bridge the current information gap between the community structure and the functional potential of microbial communities. ◆

Soils are highly complex systems in terms of their composition, dynamics, and heterogeneity with an estimated 10^9 bacteria and up to 1 km of fungal hyphae in 1 g of soil. Aggregates are the building blocks of soils, and highly stable individual microaggregates (less than 250 µm diameter) bind together to form dynamic (i.e., shorter lived), larger aggregates (2 mm diameter and larger). These individual and compound aggregates form different habitat types and are likely to feature different microbial community structures and functions. In addition, the smaller, stable microaggregates are the location of the most protected, stable carbon in the soil. As these different types of soil aggregates are what comprise the fabric of an intact soil, it is clear that the fine-scale aggregates exert a strong influence on the behavior of the whole soil. With recent advances in DNA sequencing technologies and microscale enzyme assays, it is now possible to study the diversity of soil microbial communities, the activities of community members, the functional redundancy of the community as a whole, and the community's resiliency to perturbation at the fine scale of soil aggregates (250 to 1000 µm diameter).

Because the soil carbon cycle is complex and diverse, we will focus on the metabolism of cellulose, the most abundant naturally occurring biopolymer on the planet. Enzyme assays have been developed for bulk soils, allowing the study of the entry of cellulose derived carbon into the soil through the action of microbial cellulases. Examination of the soil at the fine-scale will, however, require the development of highly sensitive fluorescence based cellulase enzyme assays to examine the activity at the scale of soil aggregates. Such an assay will provide a direct read on the functional capability of the community as well as the resiliency of that community to perturbation. The aim of this research is to integrate genomic and biochemical strategies at microscales to bridge the current information gap between the microbial community structure (phylogeny) and the functional potential of soils using soil aggregates as examples of contained microbial community "units." This analysis will provide information fundamental to the understanding of community diversity and functional redundancy in complex environmental habitats.

Specifically, we will 1) examine microbial community composition and activity at the microscale to gather information about the diversity of the aggregate community, compare the composition of communities from similar aggregates, and identify the members with cellulytic potential, and 2) identify cellulose responsive microbial species and genes under varying conditions as well as assay enzymatic reactions required for carbon entry into soil to assess the redundancy in function in aggregates of varying size classes. Soil aggregate community structure will be examined through deep coverage sequencing of phylogenetically informative ribosomal DNA regions. Current DNA pyrosequencing technology using barcoded primers provides measures of the microbial diversity and the abundance of community members. Combining this sequencing technology with stable isotope probing will allow the probing of soil aggregates to identify the active cellulytic species specifically within the community.

In FY 2009, sufficient soil samples were collected to pursue our initial focus to examine whether the microbial community structure and cellulase activity vary between soil aggregates of similar or different size classes (250 to 425 µm, 425 to 841 µm, and 841 to 1000 µm). Approximately 200 soil samples were processed for DNA pyrosequencing of the ribosomal DNA regions. These data will provide information on the prokaryotic composition of individual soil aggregates and pools of aggregates. Several samples were also processed for traditional Sanger sequencing to assess the fungal composition of pools of soil aggregates. Analysis of these data through FY 2010 will be performed in order to assess the community diversity and variability across samples and aggregates.

Additionally, microscale enzyme assays to measure cellulase activity of individual aggregates were initiated. Classical cellulase assays were scaled down to reactions in a few microliters, with the colourimetric detection of the reaction products. These microscale assays perform well with purified enzyme controls, and initial tests suggest that the assay will work with soil aggregates of each size class as noted above. During FY 2010, the generation of standard curves with the purified enzyme control and assays of hundreds of individual aggregates will provide data in order to assess the variation in enzyme activity across aggregates.

Designed Affinity Reagents with Extreme Stability and Selectivity

Cheryl L. Baird, Curt B. Boschek

◆ This project is aimed at developing a new platform for the generation of affinity reagents that possess a high degree of stability with engineered specificity for a wide range of molecular targets. Moreover, the reagents developed using this platform will be completely novel reagents with stabilities not observed in natural proteins. ◆

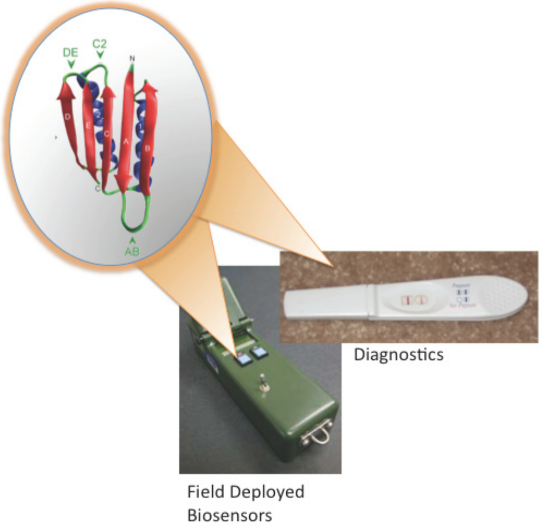
Deployable biosensors for detecting biological molecules at the source require robust selective binding molecules (affinity reagents) that can survive high temperatures and other variable conditions encountered in the field. Antibodies are the gold standard affinity reagent for protein-based detectors because of their high specificity and affinity. However, antibodies are not sufficiently robust to withstand harsh field conditions, and their interaction with their target is naturally reversible. The use of non-immune protein-based scaffolds as a basis for the generation of novel binding agents is emerging as a viable alternative to natural or recombinant antibodies.

We are using a novel protein scaffold, Top7, and covalent cross-linkers designed within the target-binding interface of Top7 to develop a strategy for engineering affinity reagents with extreme stability and infinite affinity – that is, the target selectively binds but does not dissociate from the affinity reagent. The reagents have the potential to exceed the utility of antibodies significantly in applications involving non-physiological environments where high sensitivity and specificity is required, such as field-based sensors for detecting low abundance targets in complex samples. Our goal is to create a platform for high-throughput affinity reagent production using the Top7 protein as an invariant scaffold. We will investigate the use of activatable cross-linkers to create Top7-based affinity reagents in current and developing sensor systems.

Top7 is small (12 kDa), cysteine-free, and has exceptional thermal and chemical stability. It remains folded at 98°C and has a free energy of unfolding in guanidine hydrochloride of 13.2 kcal/mol at 25°C making it considerably more stable than comparably sized proteins. We hypothesize that this rigid structure will accept insertions of binding sites with minimal disruption of the stable protein core, making it an ideal scaffold for creating the robust capture reagents necessary for field-based assays.

Our approach to engineering binding specificity into Top7 involves the creation and mining of Top7-variant libraries containing molecular recognition loops inserted at defined regions within Top7. Previously, we found that the insertion of a defined CDR into a single site within Top7 had minimal effects on the stability of Top7. This work was featured as the May 2009 cover story in the journal *Protein Engineering, Design and Selection*. Expanding on this research in FY 2009, we created a panel of libraries containing CDR loops inserted into four defined sites within Top7. Preliminary characterization of the effects of loop insertions at these sites suggests that two sites within Top7 are amenable to loop insertion without disruption of stability, while two sites are not. We are in the process of characterizing additional variants from these libraries to see if this is a consistent trend. Our work to date on Top7 provides a foundation for the future development of rapid and efficient methods for generating Top7-based affinity reagents.

In FY 2010, we will continue this effort by demonstrating the methods we have developed by generating Top7-based affinity reagents to a panel of disparate protein targets. We also plan to identify additional applications and sensors that would benefit from the high-stability of Top7 affinity reagents. For instance, antibody-based affinity chromatography is underutilized particularly in industrial applications because antibodies are frequently too expensive to be practical and cannot withstand highly reducing/denaturing environments, high ionic strength, or the pH extremes needed for column regeneration. The eventual goal of studying Top7 as an affinity reagent scaffold is to have a method available for rapidly developing an affinity reagent to any clinically or biologically useful target that is not limited in its application.



Deployed biosensors and point-of-care diagnostics would benefit from a highly stable affinity reagent such as those based on Top7.

Develop Capabilities to Study the Cellular Interactions and Fate of Nanomaterials

Galya Orr

◆ The rapid growth in nanotechnology is expected to increase human exposure to nanomaterials. These studies will identify the critical properties of inhaled nanomaterials that govern their toxicity or biocompatibility and thereby aid in formulating preventative approaches and exposure guidelines. ◆

The use of engineered nanomaterials in industrial and medical applications is expected to increase unintended environmental or occupational and intended medical or direct consumer exposures. The impact of such exposures on human health, however, is unclear. Accumulating observations demonstrate the potential of engineered nanomaterials to impose adverse effects on living systems, but a great deal of confusion remains about the properties that make a particle toxic or biocompatible. Potential nanomaterial toxicity or biocompatibility is governed by cellular interactions and particle fate, which dictate the cellular response and ultimately determine the impact on human health. These cellular interactions and subsequent responses are governed by the physical and chemical particle properties, but the relationships among these processes are far from understood.

The purpose of this project was to develop capabilities for delineating relationships between distinct properties of airborne engineered nanoparticles and their interactions, fate, and response in alveolar epithelial cells. Specifically, the goal is to establish the predictive evaluation of inhaled nonmaterial's toxicity or biocompatibility. This project focused on amorphous silica (silicon oxide) nanoparticles, which have been used in a wide array of industrial applications, potentially leading to unintended ccupational and intended medical or consumer exposures. Assays for evaluating cellular responses to amorphous silica nanoparticles with distinct surface properties have been developed, allowing the evaluation of pro-inflammatory, oxidative stress and apoptotic responses of cells exposed to distinct nanomaterials. The correlation of these responses with the specific particle properties will lead to a better understanding of the mechanisms that underlie nano-material potential toxicity or biocompatibility.

Detecting changes in the expression level of pro-inflammatory genes and proteins have been a primary approach for evaluating adverse effects. Recently, oxidative stress has been suggested as a key paradigm for evaluating the impact of nanomaterials on the living cell. Therefore, real-time quantitative reverse transcriptase polymerase chain reaction assay was established to detect changes in genes encoding pro-inflammatory protein in alveolar type II epithelial cells exposed to amorphous silica nanoparticles with distinct properties. The genes were screened at 6 and 16 hours post exposure. Initial observations showed clear increases in levels of transcripts encoding three pro-inflammatory proteins in response to positively charged amorphous silica particles and established parameters (such as dose) for further studies. These observations indicate that positively charged amorphous silica particles are capable of inducing inflammatory response at subtoxic concentrations comparable to those reported in the literature for other particles.

The uncontrolled production of reactive oxygen species has been shown to be one of the main adverse consequences of nanomaterial exposures. The assay for quantifying oxidative stress in alveolar type II epithelial cells has been established using carboxy-dichlorodihydro-fluorescein diacetate. This non-fluorescent derivative of fluorescein becomes highly fluorescent when cleaved by intracellular esterases, followed by oxidation. The exposure dose that elicited pro-inflammatory gene expression was used to evaluate oxidative stress at 24 hours post exposure. The degree of reactive oxygen species production was measured by flow cytometry. Cells were exposed to particles tagged with a fluorescent dye, and the degree of particle association with the cell was correlated with the degree of reactive oxygen species production. The established assay detected oxidative stress in alveolar type II epithelial cells exposed to positively charged amorphous silica nanoparticles, as was indicated by the increase in dichlorofluorescin fluorescence relative to unexposed cells.

The degree of nanomaterial toxicity at exposures that elicit pro-inflammatory gene expression was evaluated by assessing the degree of apoptosis at 24 hours post exposure. Fluorescent annexin V, which binds phosphatidylserine that is translocated from the inner to the outer leaflet of apoptotic cell membranes, was used to detect and count apoptotic cells by flow cytometry. The above assays will support studies for correlating cellular response with distinct particle properties, ultimately leading to a better understanding of nanomaterial toxicity or biocompatibility and contribute to the design of safe nanomateials.

Development of a Novel Cross-Linking Reagent for High-Throughput Global Analysis of Protein Interactions

Joshua N. Adkins, M. Uljana Mayer-Cumblidge, Saiful M. Chowdhury

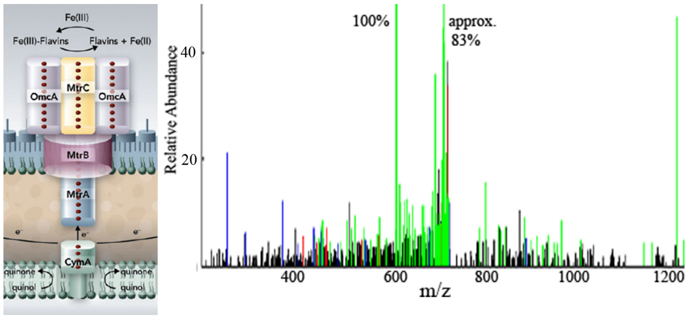
◆ This project developed chemical cross-linking and informatics methodologies to identify protein complexes—the cellular machinery of all biological systems. Technologies will yield information about cell and microbe machinery, enabling the rational pathway re-engineering to enhance hydrogen or ethanol production and carbon dioxide fixation. ◆

Energy production is a critical component of the nation's prosperity and overall security. Harnessing microbes to solve energy-related challenges and address global climate change needs holds great promise. Under current environmental conditions, microbes perform many functions that are not perfectly engineered for technological uses. An obstacle to re-engineering biological systems is a lack of knowledge of key inter-operating biomolecules. A technology, such as chemical protein cross-linking can provide a snapshot of the biological machinery under appropriate conditions. Cross-linking has been used to validate known partners in a protein complex and identify interaction sites, but not for global discovery of novel protein complexes and interactions. To harness microbes and their protein complexes for tasks such as hydrogen production and carbon sequestration, cross-linking must become a high-throughput tool that permits the rapid identification of interacting proteins in live cells.

We developed novel methodologies for global cross-linking. The long-term goal of our research is to cross-link all protein complexes simultaneously with the living cell and use mass spectrometry-based techniques to identify complex members. The process is facilitated by the small mass and a demonstrated reporter signal of the newly developed cross-linking reagent. Coupled with new informatics algorithms for identifying cross-linked species, our research builds on advances in mass spectrometry to develop a transformative technology to identify cellular protein machines.

The first practical application of methodologies developed under this project was a metal reductase membrane protein complex in *Shewanella oneidensis* and global cross-linking of the protein complexes for this organism with applications in bioremediation and biohydrogen production used in fuel cells. Data were collected for the outer membrane proteins of photosynthetic organism *Rhodobacter sphaeroides*, which fixes carbon dioxide, a gas contributing to climate change. Since this project's inception, we successfully assembled the pieces for discovering and characterizing protein complexes in intact live cells. We synthesized a novel protein cross-linking reagent CLIP (click-enabled linker for interacting proteins), synthesized a related reagent for enrichment and optimized enrichment of cross-linked species, performed mass spectrometric characterization on enriched cross-linked species, developed and applied new software for the analysis of mass spectrometric data of cross-linked peptides, and performed cross-linking experiments of complex membrane and soluble fractions.

The cross-linker was designed small to increase solubility, cell membrane permeability, and react with large protein-protein complexes. Additional features include an alkyne group for cross-linked species enrichment and a reporter mass signal. Using ubiquitin and other model systems, we confirmed selectivity of the cross-linker toward primary amine functionality. In the ubiquitin system, we identified several cross-linked species validated from the protein structure for reasonable distances between the amine-containing amino acids for which cross-links were found. This data resulted in a paper published in *Analytical Chemistry*, and a second manuscript on the bioinformatics methods is in preparation.



Left: A suspected model developed for a protein complex responsible for reduction of metals found in Shewanella. *Right: Mass spectrum of experimental data produced by our cross-linking reagent that provides unique experimental evidence for this model.*

CLIP was used to cross-link a membrane metal-reductase protein complex in *S. oneidensis*. Due to its application for bioremediation, protein function has been studied, but the relative positions remain unknown. We used new software to pinpoint where the proteins interact to explain how they function together. These same experiments were extended from the purified complex to global cross-linking in different fractions from these bacteria.

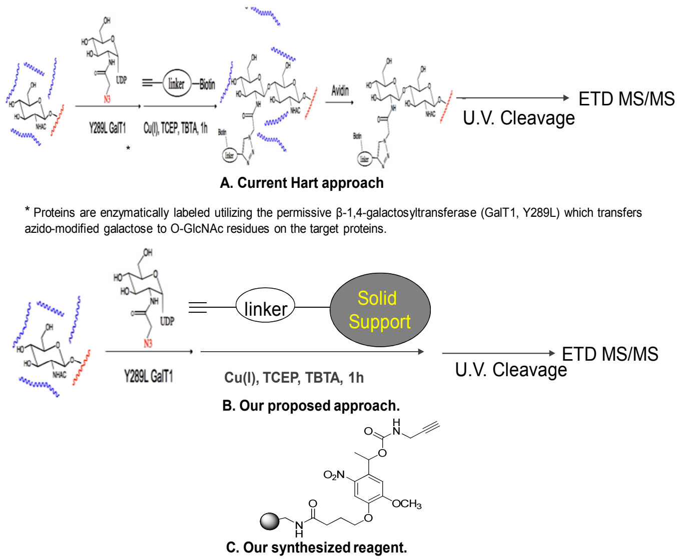
We have thus synthesized, characterized, and validated our prototype cross-linking reagent and capture validation reagent and the whole methodology. Initial data show that the cross-linker and bioinformatics programs developed in this project also apply to far more complex samples. This ability will yield information that aids the utilization of naturally occurring bio-machines toward biotechnology applications such as bioremediation, biofuel production, and carbon dioxide sequestration.

Exploration of Pan-Omics for Biological Research

Richard D. Smith

◆ This project will result in multiplexed high throughput sample processing analysis capabilities of multiple subproteomes and submetabolomes. Initial demonstrations of capabilities will extend the areas of program growth across multiple biological research areas such as carbon sequestration, bioenergy, environmental processes, biological events in response to radiation, and health related biomarker development. ◆

Our "Next Generation Measurement Platform" capabilities will develop multiplexed sample processing, pipeline development, and automation. This research will allow effective use of proteomics and metabolomics platforms and will support effective in-depth coverage of many different post-translational protein modifications or other subproteomes and submetabolomes in a high throughput manner. To achieve this objective, our initial emphases are to develop automated multiplexed enrichment technologies for effective fractionation of the global proteome and metabolome into subproteomes and submetabolomes based on their modifications and chemistry, respectively. The initial set of targeted modifications will include phosphorylation, *O* and *N* linked glycosylation, ubiquitinylation, and proteolytic processing by profiling N and C terminal peptides. Many modifications are important cell signaling and functional mechanisms.



A. Current Hart approach

* Proteins are enzymatically labeled utilizing the permissive β-1,4-galactosyltransferase (GalT1, Y289L) which transfers azido-modified galactose to O-GlcNAc residues on the target proteins.

B. Our proposed approach.

C. Our synthesized reagent.

Schemetic review of current and our proposed approaches for enrichment and identification of O-GlcNAcylated peptides.

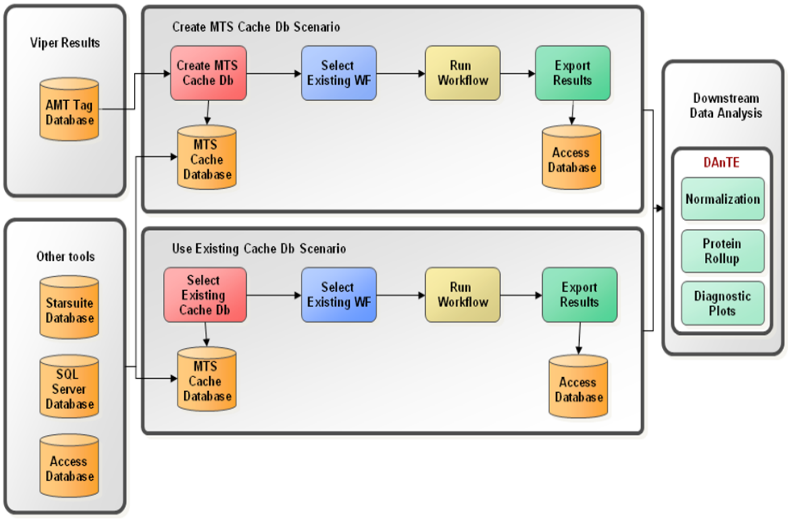
Phosphorylation. We previously developed optimized enrichment protocol for phosphorylation identification with high recovery and specificity. However, this column based enrichment is performed in low throughput, a time-consuming process. Our initial efforts on modifying the current column based enrichment protocol to the batch mode for future high throughput automation multiplexed with other enrichment technologies.

O-GlcNAcylation. Recent studies indicate that phosphorylation and *O*-linked *N*-acetylglucosamine modification (*O*-GlcNAcylation) can occur on identical or proximal sites on the same protein. The interplay of phosphorylation of *O*-GlcNAcylation may serve as a global regulation for various cellular processes. However, both enrichment and efficient identification of *O*-GlcNAcylation is challenging. The state-of-the-art work recently completed by Hart Laboratory has provided a methodology that makes it possible to characterize *O*-GlcNAcylated proteins on a large scale. In this approach, proteins are digested with trypsin, and *O*-GlcNAcylated peptides are derivatized with a novel biotinylation reagent isolated by affinity chromatography and released from the resin by photochemical cleavage. The released peptides are tagged with a basic aminomethyltriazolylacetyl-galactosamine group that facilitate their identification by electron transfer dissociation mass spectrometry.

We have been working on implementing and testing this method. Toward a more sensitive, specific approach for *O*-GlcNAcylation identification, we started using the existing enzymatic system for labeling *O*-GlcNAcylated peptides with an azido modified galactose to capture peptides with novel photocleavable reagents on various solid supports using click chemistry. The advantages of this method are: 1) eliminating the avidin binding step, thus increasing sensitivity, 2) performing extensive harsh washes, which would denature avidin to increase specificity and provide a clean sample for downstream analysis, and 3) having a simple, fast, and easily adaptation to a high throughput format with sampling preparation using solid supports such as magnetic beads.

At present, we have synthesized the first photocleavable reagent in a series on polyethylene glycol resin. We are currently testing this reagent with a commercially available model peptide. In addition, we plan on determining the extent of alkyne functionality incorporation on the beads as a means of later assessing the efficiency of *O*-GlcNAcylated peptide capture. This will be accomplished by first photo cleaving the reagent and then quantifying the resulting propargyl amine using an amine specific fluorescent assay. The photo cleavage efficiency (and thus the recovery of peptides from solid supports) will be determined using azide labeled peptides coupled with the solid supports and performing the cleavage reaction at a scale where peptide recoveries can be obtained using a simple ultraviolet assay. We will then synthesize the labeling reagent on different solid supports (polystyrene and magnetic beads) so that the influence of the solid support on photocleavage efficiency and specificity can be determined. The goal of these studies is to demonstrate the effectiveness of this detection method on peptide and protein models and then subsequently apply the method on biological samples.

The development of core informatics tools needed to enable the panomics capability includes two key areas addressed by the research that we completed in FY 2009: development of ion mobility drift time prediction capabilities and a new informatics tool that supports the management and manipulation of thousands of complex datasets.



Block diagram illustrating the MDART analysis workflow.

Predicting Drift Times. The centerpiece of the platform is the ion mobility separations coupled with time of flight mass spectrometry. This method has provided a technique for rapid, high resolution separations of analytes based upon the gas phase ion structure with significant impacts in the field of proteomic analysis. It also affords multiple improvements over traditional proteomics techniques, such as the elucidation of secondary structure information, identification of post translational modifications, and higher identification rates with reduced experiment times. The high throughput nature of this technique calls for the accurate calculation of cross-sections, mobilities, and associated drift times of peptides, thereby enabling high throughput downstream data analysis utilizing this additional dimension of information.

We developed a support vector regression based model that accurately predicts peptide cross sections directly from peptide amino acid sequence. When tested on a manually curated high confidence database of 6975 peptide sequences with experimentally measured cross sections, our prediction method yields areas with R2=90 percent for doubly charged and 85 percent for triply charged peptides. These results are statistically significantly better than the intrinsic size parameter technique (85 and 79 percent, respectively), the only other computational prediction mechanism available currently.

Multi-Dataset Analysis and Rollup Tool (MDART). MDART is a tool that allows a user to export data from the mass and time tag system into a standalone database using predefined stored procedures. Alternatively, as the software can interface with a pre existing, stand alone database in both modes, MDART allows the user to apply a workflow defining data transformation steps to process data in the stand alone database. Tables in this database can be exported to Microsoft Access or to tab delimited text files.

MDART uses an SQLite specific database to perform all of its work. Since this tool is generic, any previously generated databases can be used. SQLite was chosen for its compact size, portability, and speed at which queries perform. The workflows are stored as XML files, and the workflow editor provides a mechanism to test queries prior to running the entire workflow. The workflow editor also uses a "working" copy of the original SQLite database, which averts problems such as the accidental deletion of records or incorrect record updates made to the original database. Too, the workflow editor is a fully functional SQL editor. Because a step consists of a single SQL statement, any valid SQL statement can be executed against the database, including any deleted and updated queries. Also included is the ability to create a Pivot table (Crosstab). Finally, creating a "temporary" result table is also available. Many times when doing analysis work, the ability to query previously generated results can be advantageous.

Running a workflow is straightforward. Users would first export data into a new SQLite database or selects an existing SQLite database. Next, they would choose an existing workflow and then select the start workflow button. When a workflow is executed, a "result" copy of the original cache database is used so that the original SQLite database is preserved. This method also allows the workflow to be altered and re run using the original data. After the workflow has completed successfully, exporting results is as simple as selecting the Export button. MDART supports exporting any number of tables contained in the SQLite database to Access.

Higher-Throughput, More Sensitive Stable Isotope Probing

Helen W. Kreuzer, M. Lizabeth Alexander, Brian H. Clowers, David C. Gerlach, James F. Kelly, Jon K. Magnuson, James J. Moran, Robert L. Sams

◆ The goal of this project is to develop more sensitive, higher throughput stable isotope probing technology and apply it to a lignocellulose degrading community as a first demonstration. ◆

Stable isotope probing, an experimental approach that allows identification of microorganisms within a community that consume a particular substrate, has been a breakthrough technology that permits a culture independent association of function with phylogenetic groups. We propose to develop improved methods for stable isotope probing to enable both higher sample throughput and greater sensitivity. These improved methods would enable outcomes such as:

- the identification of key processes controlling biogeochemical cycles that sustain all life and building the knowledge base required to predict the role of microbial communities in mitigation and adaptation to global change and subsurface contamination, and
- the development of new approaches to environmentally sustainable bioenergy systems and other industrial processes.

At present, the sensitivity of stable isotope probing is limited by the methodology, which selects stable isotopically labeled nucleic acids by the buoyant density centrifugation. In order for a labeled molecule to separate from its unlabeled brethren, it must incorporate a fairly substantial amount (e.g., 20 percent) of the labeled atoms, which can obscure the detection of early incorporation events in a community. Our method is specifically directed at overcoming these problems. The approach will provide greatly enhanced sensitivity (less than 0.1 percent enrichment will be detectable), permitting the association of phylogenetic groups of microorganisms with the earliest events in the breakdown of lignocellulose and enabling a finer time resolution analysis of the process. Further, our approach should greatly decrease the time required for analysis. Although we have selected lignocellulose degradation as the experimental process to dissect, the improved technology could be applied to any microbial community and process.

In FY 2009, we simultaneously conducted a highly targeted exploration of an alternative isotope measurement approach. If completely successful, this approach could permit isotopic imaging at near single cell spatial resolution. If initial experiments appear promising, this technology will become the subject of a separate funding request to develop it fully. FY 2009 accomplishments follow.

Moving Wire Interface. At the commencement of the project, we visited the California Institute of Technology and Professor Alex Sessions, who is the developer of the Moving Wire Interface, and discussed the design with him. Following that visit, we ordered components. We also ordered instrumentation and supplies for testing the method as well as prepared or ordered RNA from several different microorganisms to serve as test materials.

Lignocellulose Degrading Community. We have started enrichment cultures using an inoculum from a large paper pulp composting operation and are feeding one cellulose and one lignocellulosic material. Our assumption is that the two communities will develop somewhat different stable populations because of the two different substrates. Eventually, we hope to compare the microbial populations as well as activities occurring within the two communities. In FY 2010, we will profile the populations and specifically characterize their substrate degrading activities.

Laser ablation and capillary spectroscopy. Initial tests of laser ablation of organic solids showed that we could ablate small particles and convert them to simple gases that are suitable for isotope ratio measurement without significant isotope fractionation. Initial testing to measure carbon isotope ratios in carbon dioxide were also promising. With equipment already in hand, we were able to measure the isotopic content of 35 picomoles of carbon dioxide. A publication is being prepared describing these experiments. Plans in FY 2010 include obtaining a new laser and new capillaries (with non-LDRD funding), which will permit further gains in sensitivity.

For FY 2010, we will develop separation methods for ribosomal RNA, construct a moving wire interface for introducing the eluant into an isotope ratio mass spectrometer, explore the possibility of collecting the eluant as a spotted array and measuring the isotopic content of the spots by secondary ion mass spectrometry, and develop and characterize an enrichment culture for lignocellulose degradation. Looking to FY 2011, we will apply the new methodology to analyze degradation of ^{13}C labeled lignocellulose by the community.

Human Exposure Monitoring for Polybrominated Diphenyl Ethers Derivatives

Irvin Schultz, Timothy J. Fortman

◆ This research is aimed at increasing our understanding of how food contaminants result in endocrine disruptions (i.e., thyroid). Ultimately, the results will be compared against groundwater and air contaminant data to assess the risk of low-level exposure to mixtures of contaminants that impact thyroid system function. ◆

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants and have become ubiquitous aquatic environmental contaminants. Direct exposure to anthropogenic PBDEs can occur as a result of release from furniture and computer products treated with flame retardants. As a result, exposure to PBDEs can affect the human thyroid system as well as cause developmental effects as described in animal models. PBDEs can be biotransformed by aquatic organisms, which complicates the assessment of PBDE health risks because a variety of PBDE derivatives (notably, hydroxylated and O-methyl esters) have been identified in edible seafood. Certain PBDEs are also marine natural products, and it is unclear (although likely) that fish, which bioaccumulate these compounds, serve as a vector for human exposures. The overall aim of this project is to collect initial experimental evidence that individuals who consume higher amounts of seafood have correspondingly higher blood levels (hence, increased internal exposure) of PBDEs and their toxicologically important metabolites and derivatives. Thus, this study will provide the critical initial data to begin identifying the potentially largest fraction of PBDEs that come from food as opposed to indoor air and groundwater.

The presence of particular PBDEs in edible seafood is of concern for several reasons. Mounting evidence indicates that PBDE hydroxylated metabolites are the most potent at disturbing thyroid hormone transport and are hypothesized to be potent agents of neurological effects. More recently, hydroxylated PBDE derivatives have also been shown to be potent inhibitors of enzymes involved in steroidogenesis and may have antiandrogen effects. Further, O-demethylation activity can be high in the mammalian liver. Thus, it is possible that PBDE-O-methyl derivatives are converted to the PBDE-OH form in humans, raising concern that consumption of fish high in PBDE derivatives may ultimately be a significant source of the toxicologically active form of PBDEs. Collectively, these concerns make it essential to understand the extent of human exposure to PBDEs and associated hydroxylated and methoxylated derivatives, and to assess whether seafood consumption is a significant source of these contaminants.

We performed a pilot study to collect exposure data in a small group of individuals (n=16) that engage in an occupation or activity that results in a high level of seafood consumption. These individuals are from the Tulalip Indian Tribe located in the northeast region of Puget Sound. Many tribal members engage in commercial or subsistence fishing activities and generally consume high levels of seafood. The PBDE levels from the tribal individuals will be compared with levels measured in a general population reference group (n=16). The reference group consists of eight men and eight women who previously participated in a study with this project's principal investigator. We have archived plasma from these individuals, which will be used for the PBDE analysis. Comparisons between the tribal members and the reference group will be made on the basis of plasma concentrations of individual PBDEs and the ∑ PBDE, ∑ PBDE-OH and ∑ MeO-PBDE concentrations.

This project officially commenced in the middle of March 2009. The first objective was to obtain approvals for our project to involve human subjects. It was decided to separate the work into two different protocols, one for using archived human plasma samples collected from a prior study and one that authorizes recruitment of new volunteers specific to the needs of this project. The first protocol was prepared and navigated through the approval process while the overall project was awaiting formal DOE approval. After mid-February and late June (respectively) protocol approvals, we contacted the Tulalip Tribal Council to seek approval in advertising for volunteers and to use the tribal health center for obtaining blood samples. The Tribal Council eventually provided approval in early September and recruitment of volunteers began. By the end of September, two volunteers enrolled. Three more volunteers have inquired about the study but are not yet enrolled. The goal was to recruit 15 volunteers; thus, additional time and more aggressive advertising are necessary to recruit an acceptable number of volunteers. We plan to continue recruiting for volunteers until the end of October.

From all of the archived samples, we performed PBDE extraction and sample clean up. Once we finish new sample collection and after subsequent extraction/clean up, we can complete the PBDE analysis. As a contingency, ten human blood samples were purchased from a commercial source. Analysis of the purchased samples will be integrated with the 16 (eight male and eight female) archived samples from white donors. The aim is to provide some preliminary data on possible variation from ethnicity.

Iterative Modeling of Host-Pathogen Interactions

Jason E. McDermott

◆ This research supports the achievement of major scientific discoveries by developing approaches for the modeling of multicellular systems. Developing tools to build useful, detailed, multiscale system models will help make progress in bioenergy, bioremediation, and carbon sequestration. ◆

Modeling biological systems requires both development and experimental validation. The more closely these two components can be tied, the more likely the endeavor will succeed. The significant amount of high throughput data available for many systems and the advent of novel, high throughput experimental techniques provide opportunities to develop detailed molecular models. These systems are difficult to parameterize because of their complexity. An urgent need remains to simplify these molecular models into functionally relevant modules that can recapitulate the systems' overall behavior. This would enable construction of large-scale models that could address significant biological questions.

Our work provides the basis for integrating different types of high throughput data into predictive models of host pathogen interactions. A multidisciplinary team was assembled to model the interaction between a pathogen and intracellular pathogenic bacterium *Salmonella enterica* serovar Typhimurium (STM) with its macrophage host, a well studied system. A large body of data both from published sources and ongoing projects were used to derive preliminary models to form testable hypotheses. In turn, results from experiments designed to analyze these hypotheses were used to refine the models. In this way, models improved and would return more useful predictions that could be tested more completely at each iteration.

This project will produce computational models of the host pathogen interaction components: STM alone under uninfectious and infectious conditions, macrophage under both conditions, and combined host pathogen interaction. Methods to partition components into functional modules and ways to link molecular components, the functional modules that they represent, and conceptual models of the infectious process for host and pathogen systems were developed. A significant outcome of this project was developing methods to link two independent models into one combined model. The techniques developed in this project will serve as a template for future models, not only for host pathogen interactions but also for any modeling projects.

The host pathogen interaction represents an attractive target for computational models for a number of reasons. Interaction between the bacteria STM and its primary target of replication in the host, the macrophage, has been studied in detail generating a wealth of high throughput data for both systems. The results of a model of host pathogen interactions could have direct and immediate impacts on human health in areas such as antibiotic drug development. Establishing an approach for multiscale modeling in multiorganism systems will impact numerous areas of systems biology.

In FY 2008, we developed computational and experimental approaches to modeling the functional and regulatory networks of STM relevant to virulence. We began to build models for the host mouse macrophage as it responds to STM infection and stimulation of the innate immune response. Additionally, we developed a number of different computational methods for deriving functional models from high throughput data, derived regulatory networks, and identified important virulence factors using computational methods. During FY 2009, we completed several tasks, including refining a functional model for pathogens including responses to environmental stimuli; finishing preliminary modeling for host macrophage cells, including signal pathways, functional modules and concept level labels; reviewing recent experimental data (both published and from collaborators) and use to refine and validate models for host and pathogen; integrating proteomics to refine the host model; completing secretome analysis and predictions to define the host pathogen interface; predicting host targets for selected *Salmonella* effectors; and combining host and pathogen models to provide a prototype temporal model of infection.

We are continuing to develop and refine previous methods, expanding their use from analysis of *Salmonella* to host analysis. We used topology of inferred networks to determine important mediators of system transitions and inferred transcriptional regulatory networks in *Salmonella* that were extensively experimentally validated. We also analyzed host response data to highlight the tumor necrosis factor-α response as being manipulated by *Salmonella* effectors. Our resulting efforts included publishing a number of high impact journal articles, including the first report of a computational method to identify type III secreted virulence effectors.

Microscale Spectroscopic Analyses of Cellulose Degradation and Uptake by a Microbial Community

Vanessa L. Bailey, Nancy J. Hess

◆ The acquisition and incorporation of cellulose derived carbon into individual microorganisms and communities is poorly understood and has not been directly observed in a measurable fashion. Complementary work at microscales will provide a new foundation for understanding the acquisition and uptake of substrates by microorganisms using extracellular cellulytic enzymes in complex spatially organized systems. ◆

Microbial communities are difficult to study. Fundamentally, they are a complex network of cells that interact at various scales to mediate a wide range of metabolic processes. They are often treated as "black boxes" in the environment, in that substrate goes into the community and various products come out. However, there is little knowledge regarding how transformations occur in a native, undefined community—i.e., whether there is any pattern or organization to the entry and assimilation of substrate into the community or how the substrate is respired. Despite the few species that unilaterally degrade cellulose completely, for simplicity, single cellulytic species will be used to initiate research on whether PNNL Raman spectroscopic techniques can track sensitively and reproducibly cellulose metabolism through microbial biomolecules at a scale equivalent to or more sensitively than has been reported elsewhere. Microenvironments that result from overlapping gradients in physical and/or chemical properties often control the location of a given microbial activity, and we need to be able to map these locations spatially in fine detail.

Cellulose degradation is attributed to extracellular enzymes secreted by the cell through processes both constitutive and induced. It is intriguing to question the contributions of these two secretion processes, as answering such a question may provide insights to the mechanisms of carbon "priming" (stimulation of the metabolism of endogenous carbon by the addition of new carbon). The use of stable isotopes in carefully designed experiments will track the entry and assimilation of cellulose carbon through the biomass. Ultimately, discerning the origin of stable and labile carbon in a community driven ecosystem would be extremely useful for land management, bioremediation featuring co-substrates, and improving our general understanding of metabolism in communities.

In FY 2009, we began optimizing spectral acquisition parameters and applying signature processing algorithms to enhance sensitivity. In the interim optimization of Raman, measurements focused both on the fabrication of a transmitted light capability to facilitate the visualization of microbial cells in aqueous media and the optimization of detector binning parameters. Prior Raman measurements relied on reflected light observation, which was adequate for observing microbial cells in air.

Model *Escherichia coli* cells were grown in minimal media, washed three times, and suspended in approximately 1 ml of distilled water. One drop of the suspended cells was transferred to a glass microscope slide and covered with a coverslip. Using the transmitted light optics individual, motile *E. coli* organisms could be easily observed using either 40 or 100x microscope objectives. Using the existing 35 mW Nd:YAG diode laser for some preliminary optimization, we found that a binning value of 3 pixels resulted in the significant increase in signal without any significant reduction in spectral resolution. The resulting Raman signal from the microbial cells was weak and had significant background contributions from the borosilicate glass slide.

The majority of the borosilicate glass contribution to the Raman signal can be removed by adjusting the confocal aperture. This option was not pursued at this time due to the low intensity of the Raman signal. Once the new laser system is installed, the confocal aperature will be optimized to minimize the borosilicate background. If adjusting the confocal aperture does not sufficiently remove the borosilicate background, we will switch to quartz glass slides, which have a lower intensity Raman signal.

Our FY 2010 goals build on the current activities to optimize the Raman capability to study the individual microorganisms using *E. coli* as the model organism as others have done. We will continue establishment of pure strains of other cellulytic microorganisms (*Cytophaga hutchinsonii*, *C. aurantiaca*, *Cellulomonas biazotea*, and *Streptomyces griseus*) for single species observation and use in mixed cultures. Further, cellulytic species will be isolated, and mixed cellulytic cultures will be extracted from soils for further work.

Modeling Nanoparticle-Cell Interactions

Brian D. Thrall, Justin G. Teeguarden, Harish Shankaran, Bobbie-Jo M. Webb-Robertson, Alejandro Heredia-Langner, Roberto D. Lins Neto, Galya Orr

◆ The goal of this project is to develop a modeling framework that bridges nanoparticle dosimetry (exposure) and cell response pathways, forming the basis for an integrated and predictive approach for assessing biological responses to nanoparticles. ◆

The initial mechanism of cell entry is a potentially important difference between how cells respond to large environmental particulates and engineered nanomaterials. Particle internalization is thought to be dependent on both particle size and surface chemistry. In particular, the internalization of large particles (i.e., greater than 0.5 μm) by macrophages has classically been associated with phagocytosis, whereas smaller particles are thought to use endocytic pathways using clathrin coated pits and caveolae rich domains. Others have suggested particles with less than 200 nm dimension can cross cell membranes through diffusion controlled processes independent of energy dependent endocytic transport. Understanding the relevant contributions of these different pathways to particle internalization is critical for understanding biocompability for several reasons. Each of these pathways operates with different affinities, kinetics, and saturation levels, and is thereby expected to dictate cell dose (and potentially toxicity) accordingly.

In this project, we are developing experimental tools and computational approaches to understand the role that specific cell surface receptors play in mediating the initial interactions between nanomaterials and cells and to determine the relationships between the surface physio-chemical properties of nanomaterials and their cellular uptake and subsequent biological response. Our initial focus is on a class of cell surface receptors expressed primarily on macrophages known as scavenger receptors. Scavenger receptors are thought to bind and internalize a large group of anionic molecules such as oxidized lipoproteins, bacterial cell wall components, and anionic particulates, thus clearing them from systemic circulation and tissues. It has been previously shown that some large (above 100 nm) particulates, such as SiO_2 and TiO_2, interact with macro-phages through scavenger receptors. However, it is uncertain whether nanomaterials utilize similar mechanisms for cell entry.

To investigate this hypothesis, model cell systems are being developed where either the expression of the endogenously expressed scavenger receptors is selectively silenced using siRNA viral transduction technologies or where new scavenger receptors are being introduced and expressed. Flow cytometry and cell microscopy, including single molecule microscopy techniques are being used to investigate the effect of receptor manipulation on the binding and internalization of fluorescently labeled nano-materials bearing different surface chemistries. We propose to develop experimental and computational approaches to describe the initial and key interactions of nanoparticles with cells that govern their cellular uptake. We hypothesize that the internalization of nanoparticles and subsequent cellular responses are at least in part receptor mediated and are influenced by the level of receptor expression and by particle surface chemistry. An understanding of these initial interactions will facilitate in the rational design of safe nanomaterials in the future.

In parallel to these experimental activities, we have developed statistically-based quantitative structure activity relationship (QSAR) models that can be used to identify quantitative and predictive relationships between the properties of chemicals and their biological effects. The QSAR models include molecular level descriptors of the particle surface physical and chemical properties with the ultimate goal of determining specific properties that dictate cell uptake and the relationships between cell uptake and cellular responses. To measure macrophage cellular responses, protein ELISA microarray analysis are being used, permitting multiplexed and quantitative analysis of a panel of secreted cytokines, chemokines and oxidative stress markers previously identified in our proteomics and genomics studies of macrophages exposed to nanoparticles. Ultimately, these QSAR models will allow us to couple the kinetic data describing receptor mediated nanoparticle uptake with multiple protein secretion profiles of macrophage activation, and provide a mathematical description of the key nanomaterial properties that drive these events.

We successfully developed mouse macrophage cell lines (RAW 264.7) where expression of the major class of scavenger receptor, SR-A1, was selectively silenced by siRNA. In addition, human cell lines (i.e., HEK) that normally do not express SR-A1 have been modified to introduce SR-A1 using lentiviral transduction methods, resulting in mutant cell lines which expressed high levels of the protein on the cell surface. These efforts provided cell models where both loss of function and gain of function studies could be performed against identical genetic backgrounds. Flow cytometry and microscopy studies have been performed using model fluorescent nanoparticles (20 to 1000 nm) to investigate the effect of SR-A1 silencing or overexpression on particle uptake and cellular response (manuscript submitted).

Specifically, time course and dose response studies indicate that the uptake of 20 nm particles into RAW 264.7 cells was significantly diminished when expression of SR-A1 was silenced to levels of approximately 10 percent of wildtype expression. In contrast, uptake of fluorescently labeled particles in wildtype HEK cells (SR-A deficient) was significantly enhanced by ectopic expression of SR-A1 protein. To our knowledge, this is the first demonstration that SR-A1 expression modulates nanoparticle internalization in macrophages. Studies using protein microarray technologies developed elsewhere have also demonstrated that silencing of SR-A1 expression diminishes macrophage secretion of proinflammatory cytokines in response to silica nanoparticles (manuscript submitted). Because the primary effect of SR-A1 silencing in these cells is to reduce the intracellular dose of nanoparticles, our results suggest that the cellular response to nanoparticles requires internalization of the particles, rather than being initiated through non-specific contact with the cell surface. Prior to these studies, the initial cellular site by which anionic nanoparticles initiated gene expression responses was largely unknown.

A molecular-level model of the predicted interactions between silica nanoparticles and the SR-A1 protein binding domain has been developed to investigate fundamental mechanisms of particle cell interactions. The SR-A1 model includes the proximal extracellular end of the receptor and was developed using homology modeling methods based on published crystallographic structures of a related scavenger receptor, MARCO. Results obtained from molecular docking studies indicate there are two primary binding sites for SiO_2 on the receptor dimer surface. These sites comprise arginine/lysine-rich “grooves” which form upon receptor folding and dimerization. To our knowledge, this is the first molecular model of interactions between an engineered nanoparticle and a specific cell surface receptor molecule developed from empirical cellular and molecular data.

Scavenger receptors, including SR-A1, are expressed throughout the liver and spleen at tissue sights where nanoparticles are known to accumulate rapidly. The speedy sequestration of nanoparticles from the bloodstream at these sights is one of the major limitations for effective application of nanoparticles as therapeutic agents. Our results provide a molecular-level explanation for how this ubiquitous class or receptors helps determine the distribution of nanoparticles in the body. Ultimately, the integrated approach we have developed will provide key insights into particle surface properties that can guide safe nano design by identifying the key properties that drive interactions with macrophages that in turn determine the pro inflammatory effects of nanomaterials.

Modeling Protein-Nanomaterial Interactions

Roberto D. Lins Neto

◆ This project aims to develop and apply computational methods to provide a molecular level understanding of the interactions that occur between proteins and nanomaterial surfaces. ◆

The development of nanotechnology has led to an increasing interest in interfacing biological molecules with nanomaterials. Proteins have been used to functionalize nanomaterials, controlling their synthesis, assembly, and influencing their properties for applications from biosensing to delivery. In turn, the surface chemistry of a nanoparticle also influences both the structure and function of the adsorbed proteins. Some specific interactions between nanomaterials and proteins in living cells have recently been shown to be cause of a series of adverse health effects. With the sharp global market increase for nanotechnology products during the next decade, the likelihood of an increased human exposure to them is also enhanced. Therefore, the understanding of the molecular basis of how nanomaterial properties affect protein structure and function becomes imperative for the design of not only smart bionanocomposites with biosensing or delivery properties but also to secure the safety of the designed nanomaterials.

To address these challenges, we will use computer simulations to characterize the influence of nanomaterials on protein conformation, functional dynamics, and stability at the nanomaterial interface as well as the underlying molecular mechanisms of interaction and adsorption. Specific project aims include identifying putative binding sites on the surface of albumin for engineered nananoparticle functional groups, characterizing the functional dynamics and structural stability of albumin adsorbed to a variety of nanoparticle surfaces, and characterizing the topography of albumin that is coated nanoparticles. Coarse grained simulations involving both multiple copies of the protein and an engineered nanoparticle will be carried out in order to assess the influence of protein-protein interactions on nanoparticle adsorption. These simulations will characterize the protein coverage and coat topography of the nanoproteome.

The results obtained in this project are expected to offer a comprehensive understanding of the influence of nanomaterial size, curvature, and surface chemistry on the structural stability and dynamics of albumin. The work will also provide a molecular understanding of the mechanisms by which nanomaterials modulate the structural behavior and functionality of proteins at the nanomaterial interface and ultimately contribute to delineate the fundamental principles of nanomaterial biocompatibility.

During FY 2009, we worked on two particular aspects of the project: 1) parameter development for the atomistic and coarse grained description of nanomaterial surfaces, and 2) the setup of large protein silica complexes. Using a combined approach of quantum and molecular mechanics methods, we have developed a coarse grained representation of a functionalized mesoporous silica nanotube. The immobilization of proteins onto these nanotubes has wide applications as biosensors. Researchers at PNNL have shown that confinement (via adsorption) of certain enzymes in functionalized mesoporous silica nanotubes can enhance the enzymes' catalytic activity.

Molecular simulations of functionalized mesoporous silica confined organophosphorours hydrolase enzyme and free in solution were performed to characterize the differences in protein structural dynamics and confirmation upon nanomaterial adsorption. Our results show that organophosphorours hydrolase adopts a slightly different configuration when adsorbed to the walls of the functionalized mesoporous silica nanotube compared with the enzyme in solution. Unlike the protein in solution, the conformation rearrangements of the material bound enzyme promote the permanent opening of a loop in the vicinity of its active site, leaving it fully accessible to substrate binding. A paper that details our findings has been submitted to and is currently under review at the *Journal of Physical Chemistry B*.

Additionally, we have developed atomistic models for goethite, crystalline, and amorphous silica. The parameters were validated by molecular dynamics simulations and density functional theory calculations. A paper describing the electrostatic cooperative effects of hydroxyl groups at metal oxide surfaces was published in the *Journal of Physical Chemistry C*. The development of these parameters has allowed us to set up large nanomaterial protein complex systems (over 150,000 atoms) to study the adsorption of albumin to crystalline and amorphous silica surfaces.

These studies will continue during FY 2010, with computational resources that have been secured by the approval of the granting of 700,000 node hours with the Environmental Molecular Sciences Laboratory's Chinook supercomputer system specifically for this study.

Module-Based Analysis of Autocrine and Paracrine Cell Signaling

Harish Shankaran, Norman J. Karin, Nikki Bollinger, William B. Chrisler

◆ The goal of this project is to construct systems level mathematical models that will reveal how cells convert information into decisions such as growth, migration, and death. A comprehensive understanding of this information processing circuitry can yield rational therapeutic strategies for diseases such as cancer. The novel engineering based modeling techniques we develop will be widely applicable to the analysis of the operating principles of complex biological systems. ◆

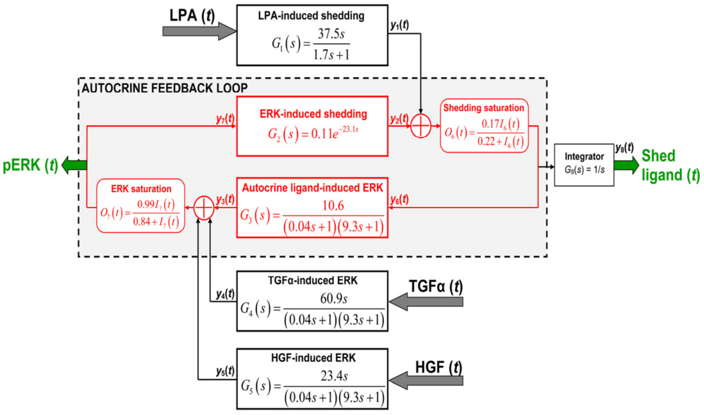
Cells process information using complex biomolecular networks involving hundreds of individual molecules called signaling networks. A commonly recognized limitation in the field of computational biology is that mathematical models that include the mechanistic details are extremely difficult to construct and parameterize, even for moderately sized networks. Hence, we propose a novel module based approach that involves the partitioning of a cell signaling network into distinct functional parts that can be studied in isolation. This would enable a hierarchical investigation of the system. At the system level, we can employ systems engineering to quantify the input/output relationships of the modules and connectivity between them. We can also construct traditional mechanistic models for individual modules of the signaling network. Inspired in part by the study of engineering systems, this hierarchical strategy will enable us to predict the effect of altering individual molecules on the entire cell signaling network.

Specifically in this project, we will apply a module based approach to understand the information flow dynamics in the epidermal growth factor receptor (EGFR) system. This involves a large number of molecular reactions and plays fundamental roles in development, tumorigenesis, responses to injury, and tissue homeostasis. The EGFR system is capable of functioning both in a paracrine fashion where inputs arrive from neighboring cells, and in an autocrine fashion, where the network is stimulated recursively in the same cell. The inherent complexity of this system and its critical role in physiological and pathological processes make it an ideal test case for the development of systems level predictive models.

In FY 2008, we constructed a linear systems engineering model that explained how the EGFR system integrates multiple autocrine and paracrine inputs. The model was trained on experimental data collected at particular input doses and was valid only as long as the inputs remained within the range of these doses. We developed traditional mechanistic models for the receptor activation module in the EGFR signaling network and a transfer function model to quantify the relationship between receptor activation and signal transduction.

In FY 2009, we refined our systems engineering model for the EGFR circuit by including saturation effects to extend to a broad range of input strengths. We showed that autocrine signaling in the circuit acts as a context dependent amplifier of external inputs. Any external stimulus is modulated to an extent defined by the strength of the autocrine feedback loop, which in turn depends on factors such as cell density and the nature of the liquid space surrounding the cell. The model was validated by comparing simulation results with new and existing experimental data for how the system responds to different inputs. Our model for the EGFR circuit is a novel demonstration of how systems engineering models can be used to understand a complex biological system.

We also constructed a detailed mathematical model for the extracellular signal regulated kinase (ERK) activation module in the EGFR circuit, one of the key downstream signaling molecules in the pathway. We used this model to explain sustained oscillations in ERK activity in response to EGFR stimulation, a feature recently discovered by PNNL researchers. We used modeling to define the regulatory structure responsible for ERK oscillations.



Systems engineering model for the EGFR circuit. Expressions in boxes (modules) are transfer functions that define how modules convert a time varying input to output. These were inferred by simultaneously fitting the model to kinetics and dose response data sets.

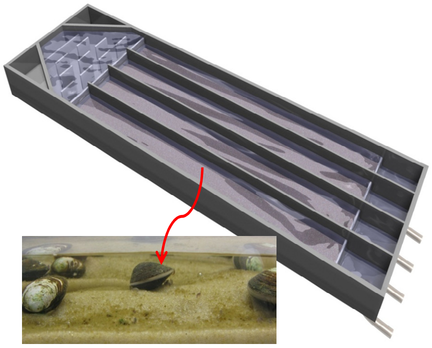
Overall, we demonstrated the utility of systems engineering models and showed how these models can be integrated with traditional mechanistic modeling approaches currently utilized in computational biology.

Nanomaterial Fate, Transport and Transformation in Freshwater Mesocosm

Amoret L. Bunn, Jill M. Brandenberger, Stephen A. Breithaupt, Marvin G. Warner, Galya Orr

◆ Release of nanomaterials into freshwater environments will increase over time as more products containing these materials become available and are discharged directly (as with antimicrobial materials) or indirectly (through remediation and municipal and industrial discharges) into receiving waters. This research is providing the fundamental information regarding the measurement, fate, transport, and transformation of silver nanoparticles in Columbia River water. ◆

Synthesized from heavy metals or carbon, nanomaterials have the potential to make a greater impact to ecological systems compared to their dissolved constituents. The smaller the particle, the greater the surface area, thus the greater potential for nanomaterials to interact with physical, chemical, and biological constituents of the freshwater environment. Beyond this, the fate of nanoparticles in riverine systems is not well understood. Studies have shown that some nanomaterials aggregate over time in Columbia River water and through biological activity. Aggregated nanoparticles could be more recalcitrant in the environment than the nano-sized material, but the processes associated with aggregating the materials may create other hazards and risks within the freshwater system.



Transport of nanosilver in a flow through mesocosm with benthic biota.

We have been developing a predictive mechanistic model to use in understanding the fate, transport, and transformation of nanomaterials in a freshwater environment. Our approach has utilized advances in material science, analytical and colloidal chemistry, toxicology, and hydrology. Work has been completed on several phases of the project: 1) development of a conceptual model to guide our research, 2) characterization of silver nanoparticles in Columbia River water and sediment, 3) evaluation of nanosilver bioaccumulation in benthic biota (algae/bacteria, amphipods, and clams) in static studies, and 4) construction, operation, and evaluation of transport of nanosilver in a flow through mesocosm with benthic biota. The information from each phase of the study has been used to build a predictive, mechanistic transport model of nanomaterials in freshwater. The outcomes of the research performed in FYs 2008 and 2009 are addressing fundamental questions about nanomaterials release into the environment and the potential risk to human and ecological health.

In FY 2008, research activities focused on basic components of the project's conceptual design. A series of static exposure studies were performed with nanosilver and a riverine microbial community and benthic invertebrate (amphipod [*Hyalella azteca*]). The microbial community showed similar response when exposed to nanosilver and ionic silver. However, amphipod results indicated that organisms were more tolerant to nanosilver than ionic silver. Investigations on size fraction and stability of nanosilver in Columbia River water demonstrated that aggregation was a function of particle concentration; we theorize that this may be a function of organic material in the river water. These results could be significant in explaining the toxicity of silver nanoparticles compared with colloidal or ionic silver.

During FY 2009, our focus was on evaluating the fate, transport, and transformation of nanosilver in a controlled, environmentally realistic flow through mesocosm system and on further model development. A benthic community was cultured in the laboratory for almost a year using Columbia River water before being transferred to mesocosms. Columbia River water was amended with nanosilver and the chemical, physical, and biological response of the system evaluated. During flow through studies, there was an insignificant loss of nanosilver to sediment, and the majority of the mass flowed through the mesocosm. Biotic uptake from the water column was observed at concentrations of 1 to 50 μg/L nanosilver. There was no apparent toxic response; however, a behavioral response was observed at the highest concentration in clams.

Comparing nanosilver results to previous research with titania nanoparticles, we learned that specific properties of nanomaterial may affect bioaccumulation and downstream ecosystem impacts. Development of a predictive model becomes challenging as input parameters depend on nanomaterial characteristics. The contrasting results of these experiments emphasize complex issues for nanoparticle research; however, successful development of a controlled, environmentally realistic flow through mesocosm system provides a tool to evaluate rapidly the multiple parameters that can be applied to predictive models. While this project is over, we plan to finalize publications during FY 2010.

PCR Arrays for Quantitative Evaluation of Microbial Communities

George T. Bonheyo, James E. Szecsody, Dawn M. Wellman, Lara M. Aston, Jason E. McDermott

◆ This project will determine quantitatively how microbial populations respond to remediation treatments. The novel methods and data generated from this project will enable scientists to transfer test tube-scale understanding to field-scale environments. ◆

Microorganisms constitute the critical interface between the fluid environment and mineral surfaces. The metabolic activities of various microbial populations are essential to many transformative processes, including those associated with biomass/carbon source conversion, pH alteration, metals sequestration, and bioremediation. However, tools are not available to quantify each of several different species in a complex environment, preventing scientists from accurately understanding or predicting environmental-scale biogeochemistry.

Our research characterizes changes in subsurface microbial communities of the Hanford Site during the course of remediation treatments. Current strategies are based on the injection of phosphate-bearing media to promote the immobilization of strontium and uranium contaminating the groundwater. Although subsurface microorganisms have potentially strong impacts on these processes, the extent to which subsurface microbial activity can modulate contaminant transport and complexation is poorly understood. Existing methods and data only measure which species are present in the subsurface and the total biomass available in a given sample (typically, well water). The tools and data from this project will enable pre- and post-treatment monitoring to enumerate individual species, characterize the transport and migration of both in situ and injected populations, identify populations (subsurface and injected) that respond and contribute to treatments, and assess how representative well water is of in situ microbial communities.

This project developed a unique capability permitting rapid determination of accurate census data for an unlimited number of microbial (bacterial, fungal, archaeal, or protozoan) species. The project initially established a comprehensive list of species inhabiting the Hanford 100 North and 300 Area sediments and pore water with supporting discriminatory DNA sequence information for each species. A smaller number of species determined to be unique to Columbia River water was also identified. The DNA sequence data was used to develop census-profiling kits (polymerase chain reaction [PCR] arrays). These tools may now be used in laboratory simulations and ongoing field-scale remediation programs to measure how microbial populations increase or decrease during treatments. The values will help identify key reactive species and allow researchers to translate bench scale analyses of single cell biochemical rates to environmental community scale process models.

Over 125 sediment and well (pore) water samples were acquired from the Hanford 100-N and 300 Areas and from laboratory simulated injection studies. Total community genomic DNA was extracted from all samples divided into three fractions, each undergoing a different extraction method. One-third of each of the three DNA preparations was archived; the remaining fraction was combined with the other two to create a composite DNA specimen for that sample. This approach increased the likelihood of successful DNA extraction from all cell types and created archival samples for later analysis. The census tools will be used to profile the archived extractions and evaluate expected biases of each method.

The extracted DNA was used in a series of PCR experiments to isolate DNA fragments that uniquely identify the various source species. Following PCR, the amplified sequences were cloned into high copy plasmids and transformed into *Escherichia coli*, resulting in the recovery of tens of thousands of cloned sequences. A total of 2112 cloned DNA fragments were selected for sequencing, and approximately 5000 reactions were conducted to determine the complete sequences that were analyzed to identify the putative source species and the redundantly isolated sequences. Unique and single representatives of repeated sequences were used to create in silico, an artificial composite sequence consisting of all unique sequences spliced end-to-end. MacVector software analyzed this “mega contig” to create pairs of unique PCR primers for each of the unique component sequences. We designed several hundred primer pairs in this manner. Given cost and time restraints, only 87 primers were synthesized; these and control primers were used to create a single 96-well microtiter array plate for use in validation and further testing.

The original 2112 sequenced clones were archived as immortal *Escherichia coli* cell lines. Those corresponding to the unique sequences in the “mega contig” were re-arrayed into a series of 96-well microtiter plates. One plate of re-arrayed clones matched the plate of unique primer pairs. A unique process was developed to test the primers using PCR assays against the suite of clones to verify specificity for the source sequences. Confirmed primers will be used in subsequent sample analyses and follow-on projects, and be the subject of subsequent invention disclosures. Once the primer sequences, methods, and findings have been published, these may be made available to collaborating scientists for continued use in analyzing subsurface communities in the Hanford Area.

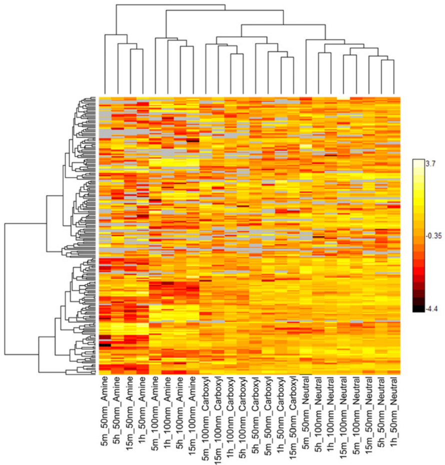
Proteomic Methods and Quantitative Structure Activity Relationship Models to Predict Nanoparticle Surface Chemistry Interactions

Tao Liu, Bobbie-Jo M. Webb-Robertson

◆ This study will enable the creation of computational models that permit predicting protein binding and provide general insight into biocompatibility with nanomaterials, an unmet need in the rapidly growing fields of nanomedicine and nanotoxicology. ◆

Protein binding plays a critical role in determining the biodistribution, clearance, and inflammatory potential of nanoparticles. While there has been intense study of protein adsorption to particulate surfaces in attempts to improve biocompatibility, previous work on protein adsorption to particles has focused on isolated, individual proteins or simple mixtures or has analyzed only a few nanomaterials, which is primarily qualitative and static. Our understanding of protein nanoparticle interactions and their biological consequences would be more advanced if we can go beyond mere identification. Of highest relevance would be information about the binding affinities and stoichiometries for different protein and nanoparticle combinations and ranking the affinities of proteins that coexist in specific bodily fluids or cellular compartments.

The overall objective of this project is to develop proteomic approaches to measure both the relative abundance and stoichiometry of nanomaterial associated proteins as well as the mathematical models to predict protein binding properties of the nanomaterials based on their surface physical and chemical properties. We will apply a multiplexed ^{18}O labeling quantitation strategy to measure accurately the differential and dynamic binding of proteins in biofluid to nanomaterials in a time course setting. Quantitative structure activity relationship modeling is then employed to formalize the physical-chemical and surface properties of nanomaterials that determine the initial interaction of nanomaterials with proteins in biofluid.



Unsupervised hierarchical clustering analysis of protein abundance data (z-score plotted) obtained by high throughput LC-MS analysis of associated proteins isolated from six different polystyrene nanoparticles incubated with human blood plasma at four different time periods (5 and 15 min; 1 and 5 h). The nanoparticles differ in size (50 and 100 nm in diameter) and surface modification (amine, carboxyl, and neutral/unmodified).

Important progress was made in FY 2008 including putting in place procedures that allow nanomaterial safety regulations and equipment to be set up in the proteomics lab for this nanomaterial-related research. A central methodological problem for studying nanoparticle associated proteins (NAPs) is to separate free proteins from those bound to nanoparticles, followed by a second step to desorb and recover NAPs from the nanoparticle surfaces. We determined that protein nanoparticle complexes can be isolated effectively and rapidly by centrifugation and repeated washing. We also developed a protocol that consists of sonication (in 1 percent sodium dodecyl sulphate), acetone precipitation, and trypsin digestion in trifluoroethanol solution for effective recovery of the NAPs for subsequent proteomics analysis. In FY 2009, we further refined the sample preparation protocol by removing the sonication and precipitation steps and using on-particle digestion, which yielded 35 percent more protein identifications while simplifying the procedures (the tryptic digestion characteristics remained unchanged).

This refined approach was applied to the isolation of NAPs from 6 polystyrene nanoparticles that differ in size (50 and 100 nm) and surface modification (amine, carboxyl and unmodified), followed by multiplexed ^{18}O labeling and liquid chromatography coupled to mass spectrometry (LC-MS) analysis. We confidently identified and quantified a total of 201 human blood plasma proteins representing the largest NAP list reported thus far. Protein binding affinities were largely independent of their initial concentration in blood plasma. In addition, unsupervised hierarchical clustering of the quantitative proteomics data showed a clear trend of the influence of different factors that may contribute to protein binding on the nanoparticle surface: charge > size > time point (shown in figure). The fastest time point (5 min) obtainable by proteomics protocols appeared to be not fast enough to capture the initial protein binding status. We then isolated NAPs from in vitro exposure of 32 different nanomaterials for analysis by LC-MS (without time point, given previous observations). The comprehensive quantitative proteomics data were used to develop and refine quantitative structure activity relationship modeling for enhanced predictive capabilities of protein binding.

Radiation Biology and Biophysics

William F. Morgan, Marianne B. Sowa, Harish Shankaran, David L. Stenoien,
Justin G. Teeguarden, Susan M. Varnum, Dulaney A. Wilson

◆ Understanding the biological effects of low dose ionizing radiation exposures will provide a scientific basis for radiation protection standards and long-term health consequences. To achieve this goal, we are exploring an integrated, systems-level approach to understand the fundamental signaling events mediated by radiation exposures, focusing on the tissue response rather than individual cells. ◆

The goal of this project is to develop preliminary data that will feed into our integrated systems level approach to understand the fundamental signaling events mediated by low doses of ionizing radiation. The focus of our work is on the tissue response rather than individual cells. The data obtained providing insights into molecular mechanisms of radiation induced signaling through the discovery of radiation associated biomarkers. Further, it will provide information on how the relative contribution of key signaling pathways is altered as exposure to radiation is protracted over long periods of time.

To date, this project has been used to develop and strengthen the laboratories' capabilities in radiation biology and biophysics. Based on data generated early in our first year, it was clear that low dose radiation investigations generated a significant amount of data. However, we were unaware of how the plethora of laboratory data would be translated to human cancer risk. To this end, funding was provided to develop computational models to predict human risk from the data generated. The frontier of low dose radiation risk sciences is developing integrated experimental and computational models of carcinogenesis and risk that embrace the underlying biology with as much mechanistic detail as experimentally and computationally tractable.

Linkage of system level mechanistic models of carcinogenesis with risk models would allow development of integrated models that relate the dose-response behavior with endpoints directly related to risk. Models such as these, calibrated to high and low-dose experimental data, will provide much more accurate predictions of risk at either lower doses or in different exposure scenarios. It is anticipated that a manuscript describing model development will be submitted in FY 2010.

For years, radiation research focused on initial responses to radiation, including DNA repair, induced chromosomal aberrations, mutations, and apoptosis. While these endpoints provide clear evidence of radiation exposure, they do not contain information on potential risk. From the initial data, it was clear that long-term effects involving persistently elevated levels of reactive oxygen species and altered cytokine/chemokine levels were also observed. Funding was used to develop antibody arrays to analyze radiation induced reactive oxygen species and cytokine/chemokine levels in our human skin samples. Such studies complement the mission of DOE low dose radiation efforts. Under this project we refined the array composition, collaborated on a manuscript summarizing the rationale, and will present a synopsis of the conceptual use of such antibody arrays in radiation research.

An important science gap is understanding radio-biological responses to low dose/low dose rate exposures to ionizing radiation in a large animal model. A significant amount of information is potentially available but in laboratory notebooks, internal reports, and annual reports to various funding agencies. A new task was thus initiated to locate, digitize, and analyze the data from beagle dogs exposed to incorporated radionuclides or external beam whole body radiation. Life span studies of over 6000 dogs were initiated in the early 1950s to investigate the effect of internally deposited radionuclides on a large animal. The experimental radionuclides were chosen from those commonly present in fallout from and production of nuclear weapons and civilian nuclear energy production. Data from these studies were compiled in annual reports from the Inhalation Toxicology (now Lovelace Respiratory) Research Institute (ITRI) in New Mexico. The goal is to "mine" these unique and important data sets and relate the cause of death to total radiation dose and dose rate. The influence of this data on life shortening, non cancer radiation induced disease and cancer following inhalation of radioactive material will also be compared with these same endpoints induced by other exposure methods, specifically whole body external irradiation. After data analysis, we will publish the information in peer reviewed literature so it will be publicly available.

By completing this preliminary task of exploring the ITRI data, we have assessed the availability of radiobiological data and a few massive sets of data for further analysis. We have also demonstrated that it is feasible to mine these data for useful radiobiological information. To achieve this goal, in FY 2010, we will focus our efforts to data mine these assembled sets for more thorough analysis, which should result in a wealth of information on radiobiological responses to low dose radiation.

Solution State Structure/Function Studies of Amelogenin Using Nuclear Magnetic Resonance

Wendy J. Shaw, Garry W. Buchko

◆ Dental enamel is the hardest tissue in the human body. It is designed to last a lifetime as it cannot be remodeled or self-repaired. Understanding the underlying biomolecular interactions of the biomineralization process initiated by amelogenin may enable dentists to repair more effectively damaged enamel. ◆

Enamel is the strongest biological material known, composed of highly ordered, unusually long hydroxyapatite (HAP) crystals. Indeed, these dental enamel crystals are over 1000 times longer than those found in bone. The proteins present during enamel development control the formation of this exquisite structure, and amelogenins constitute greater than 90 percent of this protein. Specific mutations to amelogenin and amelogenin deficient mice both result in dramatic enamel phenotypes similar to *amelogenesis imperfecta* in humans, observations that strongly suggest that amelogenin plays an essential role in amelogenesis. Molecular biology techniques have corroborated the importance of amelogenin in all aspects of enamel formation, including nucleation, growth, inhibition, and spacing. However, none of these roles is clearly understood on a molecular level.

The secondary structure of amelogenin has been studied by circular dichroism and small angle x-ray spectroscopy. The general consensus is that in the monomeric form, the tyrosine rich N-terminal region forms an extended β sheet/β strand structure, while the HAP rich region adopts a β spiral/polyproline II. This "structure" appears to be sensitive to pH, temperature, ionic strength, and metal ions. Of the many interesting features of amelogenin, perhaps the most remarkable is its ability under ideal conditions to self-assemble into a unique quaternary structure nanosphere that appears to be an essential functional, structural component of the secretory stage enamel matrix.

A 59 residue leucine rich amelogenin protein (LRAP) is the result of alternative splicing of the primary transcript, and consists of the first 33 and the last 26 residues of full length amelogenin. The two segments have been linked to specific function, as they consist of regions in full length amelogenin found almost entirely conserved across all species studied. Like the parent protein, it is observed to form nanospheres, has a strong affinity for HAP, binds a similar number of calcium atoms per molecule, and is a HAP growth inhibitor. While debate remains about its biological significance, LRAP's similarities with amelogenin make a good model, though a simpler one, necessary. The quantitative determination of the structure and orientation of full length amelogenin on a surface is not possible with currently available technology. In determining whether LRAP is a good model for full length amelogenin, we have undertaken solution state studies of the protein using nuclear magnetic resonance spectroscopy.

We assigned the ^{1}H-^{15}N heteronuclear single quantum coherence (HSQC) spectrum of murine LRAP (rp(H)LRAP) in 2 percent acetic acid at pH 3.0 by making extensive use of previous chemical shift assignments for full length murine amelogenin (rp(H)M180). This correlation was possible because like the full length protein, LRAP is intrinsically disordered under solution conditions. The major difference between the ^{1}H-^{15}N HSQC spectra of rp(H)M180 and rp(H)LRAP was another set of amide resonances for each of the seven non proline residues between S12* and Y12 at the N-terminus of rp(H)LRAP. Analysis of proline carbon chemical shifts suggest that these duplicate resonances are not from a cis-trans isomerization of one or more proline residues in the N-terminus. While the reason is unknown, the absence of such conformational exchange at the N-terminal of full length amelogenin may be a physical property responsible for the subtle biochemical differences between LRAP and the full length protein.

Using solution state nuclear magnetic resonance spectroscopy and dynamic light scattering, the initial steps of the amelogenin matrix formation were previously studied as a function of differing levels of salt, a variable that triggers protein self association. Two salts (sodium chloride and calcium chloride) were tested, both of which yielded similar step wise results for amelogenin self interaction. At low pH with no salt in the solution, amelogenin existed as individual protein molecules (monomers). Upon the addition of salt to the solution, pairs of amelogenin monomers began to interact at their N-termini to form dimers. As the salt concentration was further increased, the interaction between pairs of monomer grew stronger, as the association extended to include interactions between the C-termini.

New dimer formation is the first step in amelogenin self assembly; the full self assembly process yields amelogenin nanospheres. Similar experiments with LRAP using sodium chloride yielded similar residue specific changes in molecular dynamics, manifested by the reduction in intensity and disappearance of ^{1}H-^{15}N HSQC crosspeaks. These perturbations may also signal early events governing supramolecular self assembly of LRAP into nanospheres, supporting the use of LRAP as a model for full length amelogenin.

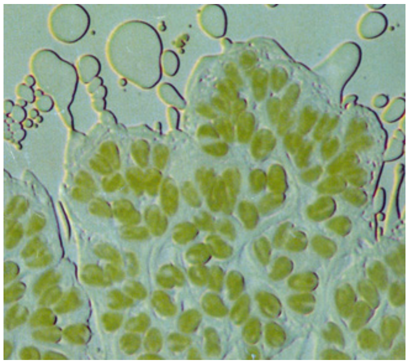
Synthetic Biology Approach for Hydrocarbon Production in Microbial Photoautotrophs

Alex S. Beliaev

◆ Through the pathways, genes, and proteins, this project assesses the means to apply genetic and metabolic manipulations to increase hydrocarbon production from sunlight and carbon dioxide. Successful implementation of this research will open new perspectives and provide a platform to design efficient, cost-effective processes for biofuel production. ◆

Using solar energy to grow photosynthetic microorganisms is one of the most attractive ways to produce transportation fuels. Among previously isolated species of microalgae exhibiting high potential for biofuel production is *Botryococcus braunii* race B (*BbB*), a green colonial microalga isolated from a variety of habitats, including freshwater and brackish lakes, reservoirs, ponds, or even ephemeral lakes. This organism has considerable potential for production of lipids and liquid hydrocarbons that can constitute a large fraction of the total biomass. The typical hydrocarbon content of photosynthetically grown cells of *BbB* averages approximately 30 to 40 percent of the dry cell mass. Hydrocarbons extracted from the biomass of *BbB* can be readily converted to fuels such as gasoline and diesel by catalytic cracking or thermochemical liquification of biomass.

Our research focuses on understanding the mechanisms of hydrocarbon production in *BbB* and embodies both scientific and technical objectives. These include development of continuous cultivation, biochemical, and genetic methods for studying the isoprenoid metabolism, which could be adapted for increased hydrocarbon biosynthesis through metabolic engineering. As cultivation of *BbB* presents a formidable challenge due to the extremely low growth rates of the organism, we focused during the first year of the project on developing tools for batch and continuous fermentation. As a result, we identified optimal conditions where cells of *BbB* grow, with doubling time of about 30 hours and display average density of 0.5 g DW/L biomass. We also developed methods for biomass collection using differential centrifugation which allows for efficient separation of *BbB* and bacterial cells. Current efforts are targeted toward the development of express screening protocol for enumeration of aggregated *BbB* cells and quantification of oils and hydrocarbons.



An organism with an interesting biology and chemistry, Botryococcus braunii *can be a blueprint for and a source of genes for the engineering organisms that produce hydrocarbons.*

The identification of *BbB* genes and proteins involved in hydrocarbon production is carried out through a combination of a combination of comparative genomic and high-throughput proteomic and transcriptomic approaches we initiated two distinct studies. We are analyzing the genome sequence and expression profiles of genes involved in hydrocarbon and (related) terpene biosynthesis pathways. The information obtained through these comparative genomic studies is being compiled into a database that we will subsequently use for targeted proteomic and transcriptomic studies. The latter will be initiated in FY 2010, as we are currently developing a collection of *BbB* samples representing different environmental conditions which affect biosynthesis of hydrocarbons. We are also focused on developing activity based proteomics approach for the identification of farnesyl diphosphate and squalene synthase enzymes of *BbB* which play a key role in hydrocarbon biosynthesis. In FY 2009, farnesyl diphosphate analogous probes to test and identify squalene and botrycoccene synthases in *BbB* were designed and synthesized. This study is conducted in collaboration with Dr. Aaron Wright, who is also developing an activity based mass spectrometry approach for studying protein function.

To achieve the metabolic engineering objective, we are developing a suitable host system that can be used for the efficient expression of hydrocarbon producing pathway. Our organism of choice is *Synechococcus* PCC 7002, for which a robust genetic system is available and a genome-wide metabolic model is being developed in collaboration with Dr. Donald Bryant of Pennsylvania State University. The metabolic reconstruction of pathways leading to production of farnesyl-PP, a key precursor for hydrocarbon biosynthesis, has been accomplished in 7002. Our approach for the engineering hydrocarbon-producing strain will be based on increasing the carbon flux through the non-mevalonate pathway and direct it toward the production of C_{30} triterpenoids using qualene/botryococcene synthases. The obstacle for the pathway will be identified using metabolomics and mutant strains.

Successful implementation of the proposed tasks opens new perspectives for designing efficient and cost-effective processes for biofuel production. Our project also provides a novel capability for the development of consolidated bio-processing methods leading to production of carbon-neutral energy at reduced economic and energetic costs.

Validation of Environmental Biomarkers in Periphyton Communities Exposed to Uranium

Ann L. Miracle, Vanessa L. Bailey, Scott E. Baker, Amoret L. Bunn,
Jon K. Magnuson, Bobbie-Jo M. Webb-Robertson

◆ A key component between biomarker discovery and application of biomarkers for risk assessment involves validation and tests of the assumptions for use of biomarkers. Validation of these candidate metrics was performed to assess the legitimacy of the biomarkers for uranium (^{238}U) exposure in periphyton. ◆

The world is facing critical issues for how to mitigate our growing population impacts on human and ecosystem health through activities involved in technology advances and energy demands. Environmental sciences previously relied on observational lagging indicators; thus, solutions have been remedial rather than preventative. Environmental biomarkers are based on measures of ecosystem response through integrated experimental designs to assess environmental responses through single molecule microscopy, transcriptomics, lipid analyses, proteomics, community diversity identification, materials characterization, and biomarker identification. Biomarkers offer the opportunity to provide early indicators of change and damage; however, they need to be relevant and valid before being applied to environmental risk assessments. In order to validate these potential diagnostic biomarkers, it is necessary to confirm that an integrated biomarker approach provides useful metrics for assessing exposure in natural periphyton communities.

This analysis provides a complete demonstration for the application of environmental biomarkers for assessing risk of ^{238}U exposure in an aquatic ecosystem. How and when a biomarker is used to provide information to decision makers on questions of interest and importance will speak to its relevance. Biomarker validity needs to be determined as a function of intrinsic qualities of the biomarker and characteristics of the analytic procedures. The integration of biomarkers of exposure and effect can provide a relevant context for assessing functional change within a complex environment and requires careful validation and systematic ground-truthing if informative biomarkers are to have prognostic and predictive power.

A ^{238}U periphyton bioaccumulation study was used to integrate the microbial community composition molecular analyses for the ecological focus area of the environmental biomarkers division. Analyses included ^{238}U uptake in periphyton, gravimetric biomass, biomass based on lipid assay, phospholipid fatty acid analysis, expressed genes through subtractive hybridization, peptide profiles, and fugal/algal identification through the Tree of Life microarray. The resulting data from each project was assessed for biosignatures that were deterministic of the exposure and could be used as potential biomarkers. These data were integrated using partial least squares, discriminant analysis, or support vector machine analysis to strengthen overall classification accuracy. The resulting candidate biomarkers showing the strongest affinity for identifying an exposed from a non exposed sample were validated using original ^{238}U and newly exposed periphyton materials.

A new periphyton experiment was conducted with three concentrations of ^{238}U, and samples were collected after 1, 2, 5, and 14 days of exposure. Water chemistry, biomass, and ^{238}U bioaccumulation were determined as in the previous exposure experiment and showed no significant changes in biomass among all samples over the duration of the experiment. Uranium uptake by periphyton was consistent with dose accumulation curves from previous experiments, and all dose targets were confirmed via water analysis.

Phospholipid fatty acid analysis profiles were determined for all replicates and time points and compared against profiles. The most discriminating peptides biomarkers and Tree of Life chip biomarkers were validated separate from the original and the new periphyton exposure material. For peptide validation, selective monitoring mass spectrometry analyses of ions (i.e., peptides) identified as biomarkers validated specific candidate peptides. The mass window was shortened ±10 Daltons of the m/z ratio observed for peptide biomarker of interest. Candidate species identified from the Tree of Life chip were validated by polymerase chain reaction using primers specific to the genera of interest. Polymerase chain reaction primers were tested against original exposed material and then used to confirm the differential presence of species in new exposure material.

The importance of validation of results is a necessary experimental step toward assurances that the data obtained and the hypotheses proposed are supported. The selected biomarkers first identified were validated in part by the phospholipid fatty acid analysis and Tree of Life chip in that several candidate markers were seen to be significant from a replicated experiment performed with materials from a different season (spring versus winter). The peptide validation was ongoing at fiscal year-end, and these results are not available at this time. However, the integration biomarker approach as validated promises to provide more accurate and complete information about functional change within ecosystems. The integration approach can be used to encourage regional preservation of resources and continued stewardship and conservation that work toward a healthy environment and clean water.

Chemistry

A Recycleable Switchable Solvent System for CO_2 Capture from Flue Gas Streams at Ambient Conditions

Clement R. Yonker, David J. Heldebrant, Phillip K. Koech

◆ The major objective of our research is to produce a reversible solvent system capable of selectively capturing CO_2 and other acid gases found in industrial gas streams. ◆

CO_2 binding organic liquids (BOLs) have been a molecularly tunable acid gas capture system for post- and pre-combustion gas streams. The technology is a liquid, non-corrosive, chemically selective CO_2 trapping agent. CO_2BOLs contain twice the CO_2 capacity and potentially half the energy to strip CO_2 chemically, compared with the industrial standards such as ethanolamine. They are more chemically selective than solid sorbents, and they can perform capture reversibly and release of other acid gases (COS, CS_2, SO_2) found in industrial gas streams. CO_2BOLs are a liquid solvent system comprised of an amidine or guanidine base and an alcohol that chemically captures CO_2. This project will investigate basic science and generate adequate knowledge required to optimize the process at the molecular-level prior to engineering and optimization on the pilot or industrial scale.

The CO_2BOL system was developed to bind CO_2 and other acid gases found in flue gas and pre combustion conditions. Once acid gases are captured, the CO_2BOL will transport the bound acid gas in the liquid phase to a release system, and then be regenerated by thermal stripping. We believe that the second generation CO_2BOL technology developed can be engineered and scaled to meet a target of 10 tons of CO_2 per day. Results achieved from this work will offer a green solvent system that can remove toxic and harmful gases from industrial gas streams. The development of the CO_2BOL technology will produce a readily reversible, environmentally responsible and recyclable acid gas trapping and transport agent.

In FY 2008, CO_2BOLs were investigated for their physical and chemical properties during CO_2 uptake. They were shown to bind and release CO_2 repeatedly with a high gravimetric and volumetric CO_2 capacity because they require no additional material to dissolve the CO_2 carrier. The investigated binding and release of CO_2 from CO_2BOLs appears to be mass transfer limited, with the dissolution of CO_2 in and out of the liquid phase being the kinetic rate limiting step. Binding of CO_2 under dilute and concentrated streams was selective, making CO_2BOLs applicable in both the post and pre combustion CO_2 capture.

In FY 2009, novel CO_2BOLs were synthesized, characterized, and tested for their compatibility with other acid gases present in flue and gasification gas streams. The technology bound repeatedly, released CO_2, and was the first solvent system to capture and release COS, CS_2, and SO_2. The viscosity of CO_2BOL materials was highly non-linear, with operating capacity optimally below 90 percent CO_2 saturation. Specific heats of the CO_2BOL system were confirmed at 40 percent that of water, and the reaction enthalpy to bind CO_2 was dependent on the chemical structure of the CO_2BOL bases. In some cases, CO_2BOLs have a CO_2 binding enthalpy as low as –60 kJ/mol, compared with –85 kJ/mol for ethanolamine. A brief cost analysis based on our measurements estimated that first generation CO_2BOL would take one half of the energy to strip CO_2, compared with a 30 percent ethanolamine system. Unlike ethanolamine, CO_2BOLs have been tunable for thermodynamics and physical properties by chemically modifying CO_2BOL components.

The binding of each acid gas to the CO_2BOL system was linked directly to the pKa of the acid to the pKa of the base component. Pairing the relative acidity of acid gas to the comparable basicity of a CO_2BOL base can selectively capture any acid gas. The fundamental understanding gained from our experiments led potentially to a chemically selective, reversible flue gas desulfurization system. The CO_2BOL base and alcohol components can be joined on the same molecule, further increasing the gravimetric capacity of each acid gas, reducing volatility, and simplifying to a unimolecular process phase chemistry. Novel second generation alkanolguanidines and alkanolamines were synthesized and characterized. These materials showed more favorable thermodynamics and multiple cycles for uptake of CO_2 and SO_2 at a reduced cost compared with first generation CO_2BOL materials. For our efforts in FY 2009, we published one manuscript, submitted another two in peer reviewed journals.

In FY 2010, the project will continue to fine tune the second generation CO_2BOLs to meet engineering requirements for post- and pre-combustion gas purification. CO_2 absorption kinetics, durability standards, and most importantly cost will be studied on a scaled up process testing system in the new user facility. Cost analysis and process feasibility will be performed with the aid of a simulated process model created by Chemcad or Aspen+. A 10,000 ton goal should be within the project scope.

An Advanced Integrated Organic Light-Emitting Devices System for Cost Effective, Efficient Solid State Lighting

Asanga B. Padmaperuma, Daniel J. Gaspar, Jonathan L. Male, Glen E. Fryxell,
Dean W. Matson, Bruce E. Bernacki, Phillip K. Koech, Lelia Cosimbescu

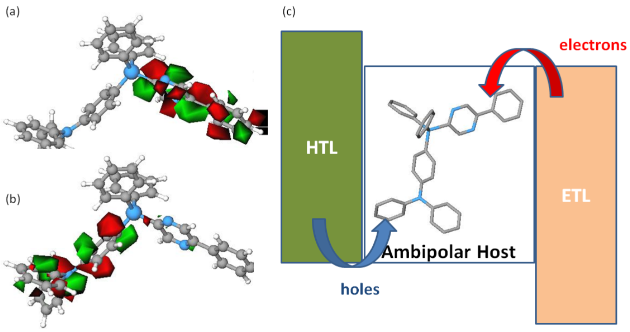
◆ We have introduced novel approaches to achieve high efficiency, long-lived blue phosphorescent-based organic light-emitting devices (OLEDs) in a practical device configuration for low cost solid state lighting (SSL) applications. This approach will be used to develop OLEDs with high quantum efficiency and low operating voltages. ◆

Long lived low-cost OLEDs with power efficiencies over 150 lm/W are essential for the widespread adoption of energy efficient SSL techniques. Currently, materials issues related to efficiency, stability, and cost prevent OLEDs from entering the lighting market. OLEDs are often schematically visualized as the analog of a *p-n* junction semiconductor, consisting of a hole injecting anode, a hole transporting organic layer (HTL), an electron-transporting layer (ETL), and an electron injecting cathode. Under the influence of a large applied electric field, charges are injected from the electrodes into the ETL and the HTL where both oppositely charged species drift to the organic hetero interface. There, the charge carriers form excitons, which decay to give light emission.

In recent years, new materials functioning as hosts, emitters, charge transporting, and charge blocking have been developed and integrated into multi-layered device architectures leading to electrophosphorescent-based OLEDs with high quantum efficiencies near the theoretical limit. However, extra layers added to the device architecture to enable high quantum efficiencies lead to higher operating voltages and correspondingly lower power efficiencies and increased complexity, failure modes, and cost. An integrated approach to design a practical, low cost, efficient white light emitting OLED has yet not emerged. A commonly overlooked factor is light out coupling—i.e., even if an internal quantum efficiency (IQE) of 100 percent was possible, the external quantum efficiency (EQE) is still limited by the efficiency of light out coupling. This work introduced novel integrated approach to achieving high efficiency, long lived blue phosphorescent based OLEDs in a practical device configuration for low cost SSL applications.

A major accomplishment of this project was setting up the capability to measure angular dependence emission spectra of OLEDs. This capability was essential to guide device fabrication for higher light out coupling efficiencies. Optimization of the charge injection layers and development of materials for blue OLEDs optimized the IQE. Even as the theoretical maximum of unity is approached for the IQE, EQE still depends on the efficiency of light extraction, improvement of which is one of the most important parameters in achieving higher power efficiency OLEDs.

We used a structure from previous work as a starting point for modeling and establishing critical performance parameters. With this information, a top emitting OLED will be fabricated to measure data needed for model input such as device dimensions, layer thicknesses, and material properties. With these initial parameters, we constructed an optical model of the device structure using commercial software. Initially, we used UniMCO40, a thin film modeling approach using dipole emission in the emissive layer with extensible material and source libraries. These modeling programs and detection setup represent a vital capability in identifying impediments and exploration strategies to enhance outcoupling.



Computationally predicted orbital of the host material lowest unoccupied (a) and highest occupied (b) molecular orbital (LUMO and HOMO, respectively) state, and schematic representation of the electron and hole injection to the host materials by the electron (c) and hole (d) transport layers.

The second task was to design and develop novel charge transporting materials to be used as hosts in blue OLEDs. Material design included a thorough computational analysis of the series of host and hole blocking materials to determine relative LUMO and HOMO energies and excited state properties. Known hole transporting moieties and electron transporting moieties were combined so that individual moieties in the final structure retain the ability to transport the desired carrier. Several target molecules were synthesized, and the molecular structure, photophysical, and electronic properties of the new materials were determined. Thermal stability was determined by differential scanning calorimetry coupled with thermal gravimetric analysis. Blue OLEDs were fabricated using these host materials, and the resulting devices demonstrated a 15 percent EQE in a representative device with no out coupling enhancements. Operational voltage was 4.2V, corresponding with a 30 lm/W power efficiency.

Banded Multiplexed Detection of Biothreats Using Superparamagnetic Nanoparticles

Richard M. Ozanich, Cynthia J. Bruckner-Lea, Kyle J. Bunch, Cynthia L. Warner, Marvin G. Warner

◆ The potential use of biological agents by terrorists is a real threat. The goal of this project was to advance magnetic nanoparticle handling approaches to enable low cost, portable devices for rapid detection of biothreats that could be used to safeguard the homeland and allow rapid response to biological outbreaks and events. ◆

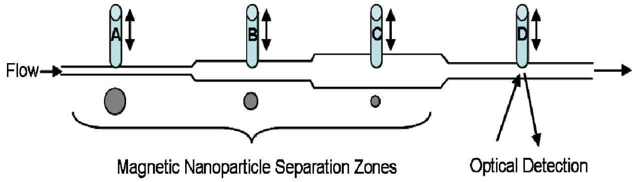
Current methods for measuring multiple biothreats in a single sample typically require complex, expensive instrumentation and are not easily fieldable. Further, these methods may result in false negative results when bioagent concentrations are very low or interfering components are present in the sample. Our research made advances in numerous areas, including:

- Developed improved protocols for nanoparticle synthesis, functionalizing nanoparticles with capture antibodies, and coupling fluorescent reporters (including quantum dots) to secondary capture antibodies
- Established procedures to validate nanoparticle size and composition, including nanoparticle mixtures, using transmission electron microscopy, energy dispersive x-ray spectrometry, and laser light scattering
- Developed an automated fluidic system, custom designed microfluidic chips, and a four stage magnetic manifold to allow automated manipulation of magnetic nanoparticles
- Evaluated over two dozen in-house synthesized and commercial nanoparticles for bioassay applicability and downselected the best candidates
- Demonstrated separation of mixtures of magnetic nanoparticles using differences in nanoparticle magnetic susceptibility
- Demonstrated the automated system could achieve picomolar sensitivity using a model sandwich immunoassay with on chip laser induced fluorescence detection.

During FY 2008, we evaluated 12 different superparamagnetic nanoparticles for assay suitability, evaluated nanoparticles capture efficiency to guide microfluidic device fabrication specifications, chose a model sandwich immunoassay based on botulium neurotoxin Type A heavy chain fragment (BoNT/A-HC), fabricated and tested an early microfluidic device design, designed and fabricated an automated mechanism for applying and removing high strength magnetic fields, and identified a novel, compact high power light source for integration with the microfluidic device.

Several key accomplishments were reached during FY 2009. Improved protocols were developed for coupling antibodies to magnetic nanoparticles and for coupling fluorescent quantum dots to secondary antibodies. The resulting reagents exhibited greater stability (e.g., less particle aggregation). In addition, nanoparticle capture efficiency was evaluated under different flow conditions and flow path geometries resulting in design and testing of several different microfluidic chips. Also, an automated fluidic system was used for testing that allowed custom fluidic protocols to be written and experiments to be executed in a highly controlled fashion. The system included a four-stage magnetic manifold that could be equipped with different size and field strength neodymium iron boron (rare earth) magnets. Finally, top performing nanoparticles were downselected but have features that will lead to rapid, sensitive assays including the ability to capture with high efficiency high antibody loading and favorable fluidic behavior.

The microfluidic system used fiber optic guided, laser induced fluorescence and sandwich immunoassay detection limits were shown to be in the picomolar range for BoNT/A-HC. Video capture of nanoparticle capture and release was used to improve understanding of the process and also revealed interesting nanoparticle behavior (i.e., release of captured nanoparticle aggregates results in uniform and complete dissolution/deaggregation thought to be the result of rapid repulsion of nanoparticles that were tightly captured together in a microfluidic channel).



Four stage microfluidic chip with four independently controllable magnets for magnetic nanoparticles separation, sequential release, and detection.

The resulting fluidics device with the automated magnet positioning manifold allowed efficient conduct of research and is a useful tool for future projects. The system allows the integration of fiber optic excitation and absorbance or fluorescence detection. This capability has broad applications in the security, defense, environmental, and clinical fields.

Carbon Nanotube Materials for Preconcentration

Jay W. Grate, Richard Zheng, Leonard S. Fifield, Norman C. Anheier Jr., David L. Baldwin

◆ Sampling and preconcentration represent significant issues in explosives detection. We propose to use carbon nanotubes as the basis of a new generation of devices for this purpose. ◆

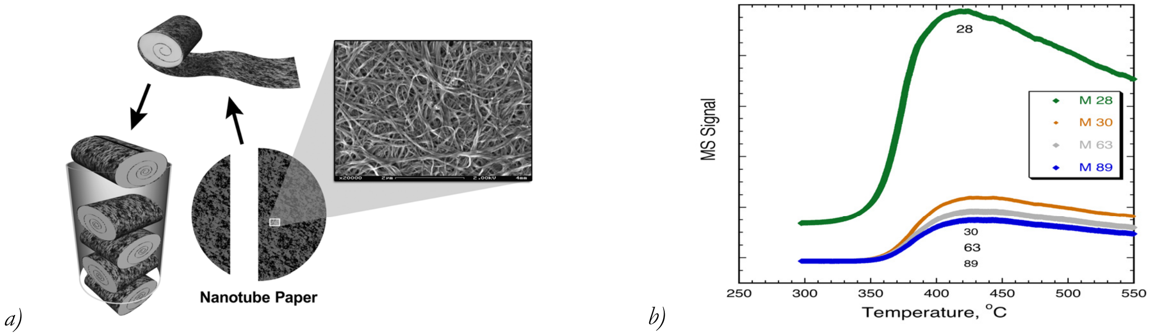
Advanced chemical sensors for trace detection are required in environmental monitoring and national security. The detection of explosives is critical to security applications ranging from defense and homeland security applications to the protection of DOE infrastructure and assets. Sampling and preconcentration represent significant issues in chemical detection in general and explosives detection in particular. Research in sorptive nanomaterials for preconcentration and sensing is essential for creating advanced sensor systems needed to meet requirements for greatly enhanced chemical sensitivity and lower detection limits. In this project, we investigated carbon nanotubes as a new material for use in thermally desorbed adsorptive preconcentrating devices. These structures and devices could be used as collectors in monitoring applications and trace detection instrumentation. In the latter case, use of a preconcentrator could reduce detection limits, improve selectivity, and/or allow other instrumentation to be used as the detector.

Carbon nanotubes have numerous desirable properties for the preconcentration of vapors in analytical applications, including high thermal stability, extremely high thermal conductivity along tube axis, electrical conductivity from semi-conducting to metallic, unique chemical interactions due to nanometer-scale C-C bonded molecular structure, unique architecture compared with most solid adsorbents (generally granular solids), being amenable to synthetic modification, and scaling ability from nanometer to micrometer to macro size applications. We anticipate several advantages and applications for carbon nanotube-based sorptive devices in chemical and explosives detection.

A unique apparatus was created in FY 2008 to perform programmed thermal desorption with real-time online vapor molecule detection. Molecules such as 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), and RDX can be desorbed from surfaces and detected. Figure b specifically illustrates the thermal desorption of 2,4-DNT from a multi-walled nanotube (MWNT) sample as a packed bed, where desorption is observed with a peak at approximately 300°C. We characterized the surface modified carbon nanotubes and investigated thermal desorption of explosives from carbon nanotubes as well as electrical methods to desorb explosives compounds.

Our approach during FY 2009 included several elements. First, we investigated a wide range of carbon nanotube materials for their thermal stability: systematic investigations from single-walled nanotubes (SWNTs), MWNT, and comparisons with carbon nanofiber materials. We determined thermal decomposition temperatures for several of these materials and demonstrated that the thermal stability of the SWNTs can be improved by purification and annealing. Next, we investigated synthetic modifications of nanotube materials. We carefully selected chemistry for altering the surface properties in ways anticipated to alter the adsorptive characteristics and selectivity. Third, we conducted investigations into the thermal desorption of explosives molecules from carbon nanotube material surfaces. These studies used thermal gravimetric analysis to determine mass loss, and vapor detection to observe the desorbed species.

Also during FY 2009, we conducted thermal desorption of pressed powders of explosives-impregnated carbon nanotubes in a vacuum system with mass spectrometry detection. These experiments detected small molecules that may arise from explosives compound decomposition on the nanotube surfaces. We found that the desorption pathways for nitroaromatic explosives compounds vary with the type of nanotube materials on which the explosive has been adsorbed.



a) Carbon nanotube paper showing an SEM image on the right, and the idea of using the nanotube paper to create a packed column on the left, b) thermal desorption of 2,4-dinitrotoluene from an SWNT with mass spectrometric detection of gases and fragments.

CO_2 Capture and Concentration Using Electrochemically Switchable Carriers

James J. Strohm, Aaron M. Appel

◆ The development of electrochemically switchable CO_2 capture methods will greatly reduce energy requirements for capturing and separating CO_2 from gas streams such as flue gas. The higher energy efficiency typical for electrochemical processes will result in lower CO_2 capture costs relative to conventional, thermally driven processes. ◆

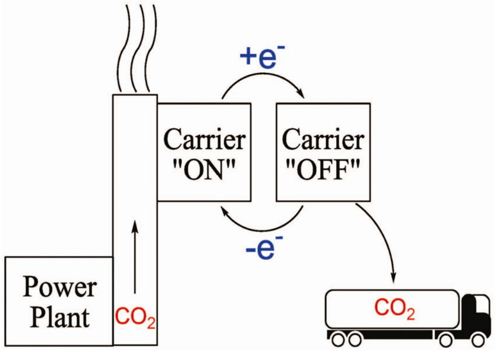
Electrochemically switchable CO_2 carriers have been previously studied but are either air sensitive or unable to capture CO_2 from dilute streams. However, the use of electrochemically switchable CO_2 carriers can greatly reduce energy requirements for capturing CO_2 – by decreasing the required energy, the cost of CO_2 capture can also be decreased. The development of new carriers is essential to the success of this general approach, and given the potential energy savings, further research is critical in order to advance electrochemically switchable CO_2 carriers into an industrially viable technology for CO_2 separations.

The goal of this project is to develop electrochemically switchable carriers capable of capturing CO_2 from flue gas streams produced by coal fired power plants. To accomplish this, we pursued two basic lines of research: we used existing electrochemically switchable CO_2 carriers to study the general approach and answer basic questions about flow reactor design, and we have investigated new carrier classes. Our dual approach has allowed study of the whole process while pursuing improved chemistry, thereby enabling simultaneous advancement in both areas. Electrochemically switchable CO_2 carriers were previously demonstrated on a laboratory scale in batch but never in flow reactors, which are generally preferred for large-scale industrial applications. Therefore, we constructed and operated flow reactors using a previously developed carrier. These reactors demonstrated that the process works in a continuous reactor, plus they were developed to answer fundamental questions about electrochemically switchable CO_2 carriers.

In FY 2008, a simple flow reactor was constructed to demonstrate that a flow reactor could be utilized, and this was successful. However, the operating potential was very poorly optimized largely due to cell resistant, so an improved flow reactor was constructed in FY 2009. This reactor was equipped with gas analyzers, flow meters, and data logging capabilities, and the reactor design and electrode layout was improved, leading to substantially lower resistances. Additional work needs to be performed to optimize this reactor operation, including improving the gas/liquid separation at the electrode assembly.

While the carrier used in the flow reactors allowed for demonstration of the overall approach in continuous reactors, this carrier is not suitable for operation in the presence of oxygen and therefore cannot be used for CO_2 capture from post combustion flue gas streams. Therefore, improved carriers have been pursued. Multiple avenues have been considered and investigated; however, in FY 2009, a simpler and more general approach was developed that would greatly reduce the cost of the carrier, decrease the overall current requirements, and allow for more generalized carrier development. This approach shows great potential but needs further development.

For FY 2010, we will develop electrochemically switchable CO_2 carriers based on the new approach developed in FY 2009. A wide-range of potential carriers are possible, so initial efforts will focus on the development of carriers analogous to the specific chemistry developed in FY 2009 but will expand to other promising avenues. The performance of new carriers will be quantified using multiple techniques, particularly to determine current requirements, potential energy efficiencies, and reversibility. Additional electrochemical expertise will be utilized to investigate new systems and approaches.



Capture of CO_2 from a flue-gas stream using an electrochemically switchable CO_2 carrier.

In addition to the development of new electrochemically switchable CO_2 carriers, additional refinement of the FY 2009 flow reactor is needed. Specific research needs include the construction of better electrode assemblies from suitably corrosion resistant materials as well as operational testing and optimization of the flow reactor. Optimization of electrode areas and configurations are the keys to achieving high current densities as well as efficient gas/liquid separations. The reactor development and optimization efforts will continue to utilize existing carriers until improved carriers are ready for testing in a flow reactor.

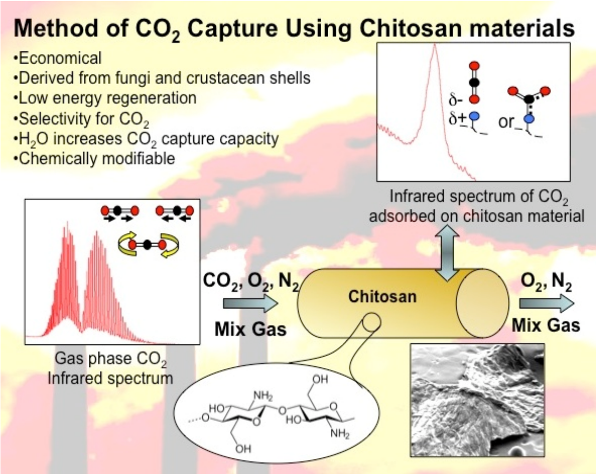
CO_2 Separation and Capture by Chitosan Materials

Tatiana G. Levitskaia, James M. Peterson, Amanda J. Casella

◆ This project will result in developing new and unique chemistries and treatment methodologies that enhance and strengthen our ability to reduce the impact of carbon dioxide (CO_2) on the environment. The benefit of this research is a proof-of-concept that commercially available, large-scale, safe, non-toxic amino sorbent chitosan can be used for CO_2 separation and capture. ◆

Investigation of new approaches for the separation and capture of CO_2 is high priority research. The goal is to isolate CO_2 from its many sources in a form suitable for transport and sequestration. The process is based on principles of chemical absorption using monoethanolamine or diethanolamine and is considered as a highly promising technique for capturing greenhouse gas emission from flue gas streams. The costs, including compression to the required pressure for the sequestration step, are estimated to comprise three-fourths of the total cost of ocean or geologic sequestration. Their improvement will reduce the total cost required for sequestration. This project will test commercial amino sorbent chitosan for the capture of CO_2 from gas streams.

The technical merit of our approach is two fold: 1) chitosan materials have been previously shown to exhibit high affinity for CO_2, and 2) they are readily available, economical, safe, durable, easily regenerable, and can be used on industrial scale. A polysaccharide manufactured from fungal sources or waste shells of crab and shrimp, chitosan is produced on a large scale by hydrolysis of chitin and is composed of β-(1-4)-linked N-acetyl-D-glucosamine residues. It is one of the most abundant, available and renewable natural biopolymers, second only to cellulose. Chitosan materials are readily available, economical, safe, durable, easily regenerable, and can be used on an industrial scale. They exhibit hydrophilicity, good chemical, temperature/pressure, and mechanical resistance properties. An important advantage of chitosan is that it can be engineered into different physical forms such as nanoparticles, microspheres, membranes, sorption beads, and the like. Additionally, because of its amino and hydroxy functionalities, chitosan is amicable to chemical modifications such as cross linking, which can be implemented as needed to control its surface area, pore size, and chemical and mechanical properties. We hypothesize that chitosan efficiently captures CO_2 due to its high amino nitrogen content.



CO_2 separation and capture by chitosan: validation using infrared spectroscopic measurements.

In FY 2009, our research focused on demonstrating that chitosan can be used for efficient and selective uptake of CO_2 from flue gas. Several commercial chitosan samples were characterized for physicochemical properties. It was determined that chitosan is thermally stable up to about 220°C and thermally decomposes around 290°C, which satisfies requirements for the flue gas applications. The unmodified commercial chitosan exhibits low surface area ranging from 0.3 to 0.9 m^2/g, and has an average water content of 5.4 wt%.

Isothermic CO_2 sorption experiments using several chitosan materials were performed in a pressure vessel, with desorption analyzed by a gas chromatography-mass spectrometry technique. In the 25 to 65°C temperature range, CO_2 uptake by chitosan after 24 hours of sorption was quantified to be on average 0.55 wt% (0.0055 g of CO_2 sorbed by 1 g of chitosan) with most of the uptake taking place within the first 3 hours. Fourier transform infrared spectrometry measurements confirmed CO_2 chemical sorption by the amino functional groups of chitosan through the appearance of a unique peak in the CO_2 region. Chemical sorption resulted in the fixing of the characteristic rotational structure of the anti symmetrical stretch seen in the gas phase CO_2 molecule to a single band shifted to lower energy.

Selectivity studies performed with a gas mixture of CO_2, O_2, and N_2 demonstrated that chitosan selectively captured CO_2 while having little affinity or being hindered by the O_2 or N_2. Another interesting finding was that an increase in the water content, such as is present in flue gas, in chitosan significantly enhanced the CO_2 sorption. Based on these results, we concluded that chitosan exhibits high potential as an affordable and effective material for CO_2 separation and capture. Our research could significantly expand currently limited options for CO_2 separation and capture from a flue gas using a readily available and economical solid amino sorbent.

Combinatorial Operando Catalyst Research

David L. King, Guosheng Li, Dehong Hu

◆ The main objective of this project was to build a combinatorial operando system for accelerated catalyst research and to demonstrate the capability in one or more applications. ◆

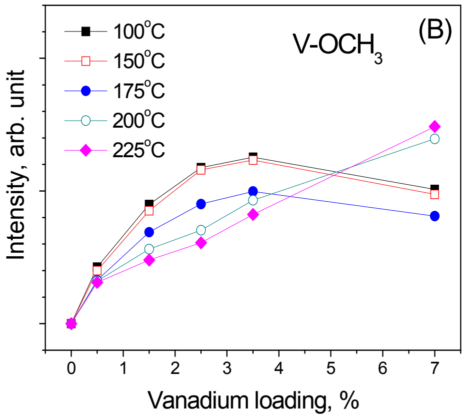
The combinatorial operando catalyst research (COMBOCARE) system is the first of its kind with unique designs capable of operating at high temperature and pressures. It integrates Fourier transform infrared and Raman imaging techniques jointly to a combinatorial reactor assembly for real-time full product analysis and material characterization under operating conditions. The system is able to characterize the adsorbed molecule catalyst interaction, reaction precursor intermediate states, and site structural variations while providing a unique high throughput reactor assembly capable of evaluating multiple catalysts simultaneously. The primary aim of the proposed COMBOCARE is to enhance capability in combinatorial catalysis. It builds on a combination of our technical expertise in catalysis, material synthesis, reactor design, spectroscopic imaging, and high throughput knowledge. Such a system is expected to be heavily used for exploratory research in materials and catalysis, rapid idea verifications, accelerated project execution and delivery, and informatics development toward rational catalytic material design.

In FY 2008, the COMBOCARE system focused on relatively simple oxidation reactions (methanol oxidation) that could be carried out at relatively low temperature and atmospheric pressure. Work involving V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts identified key catalyst surface species via the Raman capability, and this work was presented at conferences and published.

Prior to 2009, the COMBOCARE system used Raman spectroscopy to characterize the catalyst surface and infrared spectroscopy in the gas phase for monitoring of reaction products. In 2009, this system was augmented through the addition of a gas chromatography system for quantitative analysis and a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Where the Raman capability functioned primarily to characterize the catalyst surface (oxidation states, phases), the introduction of DRIFTS increases the capability to analyze active reaction intermediates and byproducts coming from the chemical reaction itself. The COMBOCARE system is available and capable of 1) monitoring high throughput parallel reactions, 2) analyzing simultaneous, continuous real-time of all product streams, 3) characterizing continuous real time of catalysts and surface intermediate species, and 4) applying to gas and condensed phase processes.

Also in 2009, a substantial effort was made to modify the COMBOCARE system to allow for elevated pressure and temperature operation, giving the system greater flexibility to examine catalyst systems of greater relevance to much of the work in energy-related catalysis that is carried out at PNNL. One reaction that was examined with this update system was the hydroformylation of ethylene using silica supported Rh-based heterogeneous catalysts.

The reaction mechanism of methanol oxidation catalyzed by vanadium oxides on a silica support (V_2O_5/SiO_2) was investigated in a high-throughput operando reactor that consisted of Fourier transform-infrared imaging for rapid product analysis and parallel, in situ Raman spectroscopy for catalyst characterization. The V_2O_5/SiO_2 catalysts with different vanadium loadings (i.e., from 0 to 7 percent) were simultaneously monitored under identical experimental conditions. The specific Raman bands of the different catalysts in the six parallel reaction channels are quantitatively compared in this paper. Under steady state reaction conditions, the Raman intensities of C–H stretch for Si–O–CH_3 and V–O–CH_3 were extensively studied at different reaction temperatures and different vanadium loadings. For the first time, we observed enhanced Si–O–CH_3 formation on V_2O_5/SiO_2 catalysts with low vanadium loadings. We attribute this phenomenon to surface cluster edge activation. Careful comparison of the in situ Raman intensity of V–O–CH_3 on V_2O_5/SiO_2 catalysts revealed different methoxy formation mechanisms in different reaction temperature regimes, as shown in the figure. The results of silica supported vanadium oxides have been submitted to *Topics in Catalysis*.



Intensities of C–H stretch Raman bands V–OCH$_3$ with increasing vanadium loadings under the different reaction temperatures.

Enhanced Explosive Signature Capture via Selective Collection and Preconcentration Chemistries

J. Tim Bays, R. Shane Addleman

◆ We propose to develop novel, functionalized nanomaterials to test against existing systems for the selective capture of volatile airborne explosive signatures. This will support the rapid collection and unambiguous identification of explosives signatures in real-world operational environments that require a tireless, rapid, sensitive, selective system not prone to false alarms. ◆

The detection of explosives is critical to security applications that range from defense and homeland security applications to the protection of DOE infrastructure and assets. Detection of explosive vapors is difficult because most of the explosives have low vapor pressures and/or are sealed inside a container, severely limiting access to the any signature compounds. Detection of explosives via detection of their vapors is viable as demonstrated by research with dogs. However, current atmospheric detection techniques are prone to false positives because they have poor selectivity and insufficient sensitivity. Improving sample cleanup through selective pre-concentration of explosive signature vapors will lead to enhanced detection sensitivity and accuracy. Additionally, improved sampling and preconcentration represent significant means to improved explosives detection.

In this project, we have developed novel functionalized nanomaterials and tested them against existing systems (e.g., activated carbon and stainless steel grips) for the selective capture of volatile airborne explosive signatures. Upon completion of this work, we will have gained an understanding of the impact of the nanostructure and surface chemistry upon collection of low volatility explosive signatures. We will use this knowledge to develop superior materials for the capture of explosive signatures. This will also support the rapid collection and unambiguous identification of explosives signatures in real-world operational environments that require a tireless, rapid, sensitive, selective system not prone to false alarms.

For this project, we synthesized over 100 different surface chemistries for explosive collection and evaluated them against presently available standard commercial materials. The affinity and stability of surface chemistries for DNT, TNT, and RDX were measured with thermogravimetric analysis. A number of new surface chemistries were identified as having good affinity to enhance explosive signature collection as well as the stability necessary to support collection analysis. The comparative testing showed that these surface chemistries were significant better than existing commercial material surfaces.

In FY 2009, we demonstrated that careful integration of the correct physical structure with new surface chemistries can provide enhanced collection and detection of selected explosives signatures. Methods to graft these surface chemistries to a range of relevant cloth supports were developed to enable demonstration on relevant analytical systems. Specifically, we made and tested surface modified cloth swipes for improved surface collection of explosives (as performed during baggage screening at airports). We found that not only were surface modified swipes analyte collected, but also showed improved detection when used with typical field instruments (i.e., ion mobility spectrometer). We also found that appropriately modified nanoporous ceramic powders provided better collection of trace level explosives (such as TNT) than conventional materials (such as activated carbon and organic resins). We demonstrated that modifying and enhancing the vapor collection of steel wires were analogous to those used for portal monitoring. Finally, we installed nanoporous thin films on glass and steel fibers to increase their surface area by more than 100 times.

We then installed the high affinity surface chemistry to provide improved selectivity and affinity for vapor collection. The surface modified wires were thin evaluated and demonstrated using solid phase microextraction, which is routinely used for rapid trace level sampling and analysis of organic compounds. The microextraction fibers adsorb a class of analytes when exposed to either liquids or gases, put into a thermal desorption gas chromatograph and read out. This approach is convenient and supports rapid analysis, but performance is based on solid phase micro-extraction fiber surface coating efficacy. We demonstrated that our materials provide significantly better performance than commercial materials. In one specific DNT signal to SPME example, we used comparative signals from DNT vapors collected on a commercial polymer coated to a bare metal wire to a wire that was coated with an unfunctionalized nanoporous silica thin film (NPFT) and an NPFT functionalized selective surface chemistry. Our results clearly demonstrated that the NPFT provided better capture of DNT vapors, up to nearly 10 times that of commercial material.

In summary, we have developed and demonstrated new surface chemistries and integrated onto nanostructured supports to enhance detection of trace levels of organic compound in general and explosives in particular. With select applications, these hierarchical materials enhance sampling and measurement.

Enhanced Ion Detection Mechanisms for Ion Mobility Spectrometry

Brian H. Clowers

◆ Despite its resounding success as a field-based instrument for explosives detection, ion mobility spectrometry relies on very few core principles centered in ion generation and gating, as well as signal detection. In an effort to leverage recent developments in these core technologies, this project aims to enhance the detection mechanism to produce a higher level of security through field-based measurements. ◆

In addition to being mechanically robust, ion mobility spectrometry is a rapid gas phase separation technique that provides a high degree of selectivity and sensitivity for a range of gas phase analytes. Consequently, it is widely used throughout the world as a field based method for the detection of narcotics, chemical warfare agents, and explosives. However, the technology used in commercial systems has remained largely static since its introduction. Over the last 30 years, a number of technical developments have been realized with respect to signal detection but have yet to be examined thoroughly in conjunction with ion mobility spectrometry. In order to bolster the absolute detection limits and maximize the utility as an explosives detector, we aim to explore the use of two general approaches to enhanced signal detection. The first focus area is directed toward the absolute noise reduction in signal recording mechanisms, and the second seeks to explore the practicality of signal amplification at pressures that approach ambient conditions.

During FY 2009, our primary task included developing the infrastructure necessary to conduct low current measurements with a specific focus on explosives detection. In addition to the design and construction of a research grade ion mobility system, the support for exploring noise reduction mechanisms and signal amplification at elevated pressures was needed. Originally, the focus on absolute noise reduction and signal amplification was to be accomplished using capacitive transimpedance amplifier and electron cascading mechanisms, respectively. However, a previous institutional investment in another approach to the design of the instrument has been identified that is better suited to absolute noise reduction and direct current measurements than capacitive transimpedance amplifier technology.

Initial results using electronics designed for single channel measurements have been conducted and have demonstrated the ability of this design to measure picoamps of current without the aid of external amplifiers and signal filters. In order to adapt the design for ion mobility spectrometry, we invested in the design and construction of sensor electronics capable of measuring current simultaneously. The prototype detector design for the new approach has been constructed using standard printed circuit board materials but will be upgraded to materials designed for high temperature following a more detailed examination of the prototype design during FY 2010.

The pursuit of ion mobility spectrometry detector technology that directly circumvents the need for external high speed current to voltage converters has focused on identifying the high pressure conditions necessary to induce electron cascading. While the conditions necessary to achieve high pressure electron cascading can easily be demonstrated within the laboratory, the primary challenge lies in the ability to quench the cascading event so that subsequent measurements can be performed in rapid succession. In order to meet this challenge, we have identified a unique micro-fabricated detector designed specifically to address these concerns.

Also in FY 2009, we completed the design and parts fabrication of ion mobility spectrometry, with significant progress made toward the final assembly of the research grade ion mobility spectrometry system. In addition to the physical apparatus itself, the next generation of ion mobility spectrometry electronic and software controls have been developed and tested. These controls are applicable not only to our current work but also to future ion mobility spectrometry projects. While all of the goals we outlined for FY 2009 were not fulfilled in their entirety, we made significant progress toward the implementation of a multi-functional ion mobility spectrometry system designed to assess all of the new detector technologies. In addition, our efforts allowed us to narrow the focus on the two detector technologies that showed the great promise toward generally enhancing explosives technology through ion mobility spectrometry specifically.

A parallel objective in FY 2010 is to provide a thorough summary of the tested detection technologies and their performance under atmospheric pressure conditions. A more comprehensive understanding of operating conditions required for new detector technologies will allow a more complete assessment regarding the potential for field based applications. We will produce a functional laboratory prototype ion mobility spectrometer that incorporates the most recent technological advances in high pressure ion detection. While the primary target of detection for this new class of detectors will be explosives, it is anticipated that the application will be extended and applicable to related areas of interest.

Fundamental Understanding of Carbohydrate Catalyst in Ionic Liquids

James A. Franz, Guosheng Li, Donald M. Camaioni, Bojana Ginovska, John L. Fulton

◆ This project develops catalysts for use in a novel process to convert cellulosic biomass in an ionic liquid medium to a key building block molecule (5-hydroxy-methylfurfural; HMF) for production of transportation fuels (gasoline and diesel). This technology is truly transformational in scope, making possible the replacement of as much as 30 percent of U.S. petroleum resources with biomass-derived carbon in a non-biological process. ◆

Cellulose is known for its difficulty of conversion to monomeric chemicals by chemical means. Simple acid hydrolysis is slow and results in low yields of desired glucose and significant degradation to unwanted products. In contrast, this program has shown that cellulose can be converted to a mixture of monomeric materials in substantial (55 percent) yield at rates more than 10-fold faster than simple acid hydrolysis. Previous to this study, no satisfactory catalytic method for the conversion of cellulose to glucose and related monomeric products had been developed.

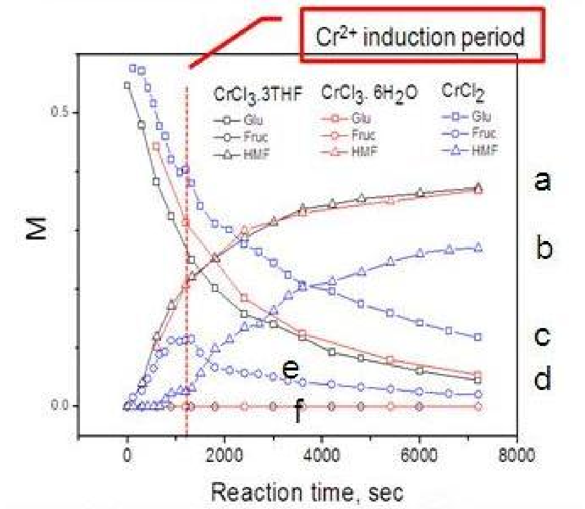
Using combinatorial catalysis, this study showed in FY 2008 that a mixture of copper and chromium, iron, or palladium chlorides catalyzed the hydrolysis of cellulose to glucose and other products. It was additionally learned that chromium chloride catalysts catalyze the conversion of glucose to fructose and HMF. Based on a combinatorial search of candidate metal chlorides, these two major empirical discoveries form the basis of a process for converting cellulosic biomass to glucose and glucose to fructose and HMF. HMF is a valuable molecule that can be converted to an important blendstock for use in gasoline or diesel or for further refining. While groundbreaking, FY 2008 discoveries produced rather modest yields of conversion of cellulose and glucose. Cellulose was converted in yields approaching 55 percent to a mixture of monomeric substances, and glucose could be converted to HMF in up to 65 percent yield. Higher yields of conversion and improved selectivity is desirable if an industrial process is to be designed around these discoveries.

The scientific approach taken in FY 2009 was modified from one of empirical discovery to one oriented toward discovery of a scientific basis for the discoveries, so that rational catalyst design could be based on an improved mechanistic understanding. Further work to understand the mechanism of copper, chromium, and palladium halide catalyst action was carried out, beginning with scrutiny of the mechanism of conversion of glucose to fructose and HMF. The study resulted in major improvement in both kinetic rates, selectivity, and yields of conversion of glucose to fructose and HMF by developing a detailed description of the nature and function of chromium chloride catalysis. It is important to understand that previous technology was based on conversion of fructose to HMF. This represented a significant bottleneck removed by this study to the utilization of biomass because the technology requires the conversion of glucose (the primary monomer of cellulosic biomass) to HMF.

A combination of structural, kinetic and theoretical electronic structure calculations were undertaken to understand the actual catalyst structure and function involved with Cr(II,III) halide catalysis of conversion of glucose to HMF. Key discoveries were made with chromium halide catalysts that led to significantly improved rates and yields of conversion of glucose to HMF. By selecting appropriate Cr(III) catalyst precursor structures, the rate of conversion of glucose to HMF was tripled, and the percent conversion of glucose to HMF was increased from 65 to 80 percent.

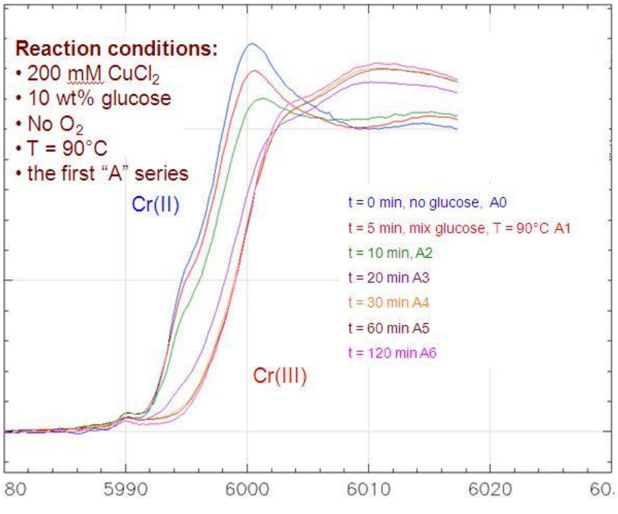
Studies during FY 2009 identified Cr(II) chloride as the most highly active catalyst in conversion of glucose to HMF. We employed x-ray absorption fine structure (XAFS) and x-ray absorption near edge spectroscopy (XANES) to determine the actual structure and oxidation state of chromium during glucose conversion in the ionic liquid ethylmethyl imidazolium chloride (EMIMCl). Chromium EXAFS and EXANES experiments were carried out at Argonne National Laboratory, revealing that Cr(II) is rapidly converted to Cr(III) in the presence of glucose and in the absence of air. Further, parallel kinetic experiments with Cr(II) chloride catalyst precursor revealed that conversion of glucose to HMF proceeds slowly, until all of the Cr(II) is converted to Cr(III). These results suggested that Cr(III), not Cr(II) as suggested by FY 2008 studies, was the more favorable catalyst precursor. It was also revealed that $CrCl_3$ was slightly soluble in the ionic liquid medium, limiting its effectiveness as a Cr(III) precursor.

With this information in hand, new soluble Cr(III) catalyst precursors $CrCl_3 \cdot 3THF$ and chromium trichloride hexahydrate, $CrCl_2(4H_2O)Cl(2H_2O)$, were selected. These Cr(III) precursors formed working catalysts that were three-fold faster than the previous Cr(II) precursor, exhibited no inhibition period, and resulted in substantially improved yields (80 percent) over the previous Cr(II) system. EXAFS studies of the evolution of catalyst structure from the two Cr(III) precursor systems revealed that the coordination sphere evolved from a chromium center with approximately four chloride atoms to a chromium center with a reduced number of chloride ligands and additional water or hydroxide ligands.

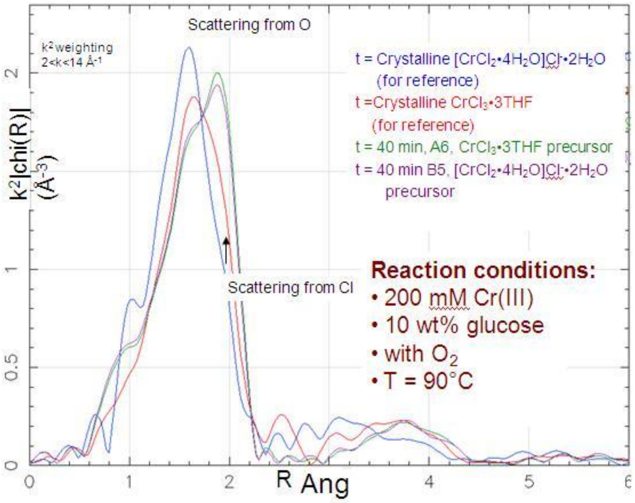


Kinetics of conversion of glucose to HMF in EMIMCl ionic liquid: a) enhanced rates and yields of HMF from Cr(III) precursors compared to b) HMF production from Cr(II), showing induction period where Cr(II) converts to Cr(III), c) disappearance of glucose with Cr(III) and Cr(II), d) enhanced conversion of glucose with Cr(III), e) appearance and disappearance of fructose with Cr(II), and f) greatly enhanced rate of conversion of fructose, which does not accumulate as an intermediate with Cr(III).

As shown in the above figure, rates and yields of HMF are greatly enhanced with discovery of the new Cr(III) catalyst precursors. The important role of Cr(III) and the conversion of the Cr(II) catalyst precursor $CrCl_2$ is depicted in the EXANES spectra in the figure below. The evolution of the $CrCl_2$ catalyst precursor to a Cr(III) catalyst is demonstrated and explains the induction period observed for HMF formation observed in detailed kinetics of HMF glucose conversion. The conversion of different homogeneous Cr(III) catalysts yield an identical intermediate structure, as shown by XAFS.



EXANES near edge spectra reveal Cr(II) to be converted to Cr(III) in EMIMCl in the presence of glucose as time progresses from left to right.



XAFS spectra show both $CrCl_3$.3THF and $CrCl_3$.6H_2O form an identical Cr(III) structure in EMIMCl that has four Cl ligands. Upon generation of water from glucose, Cl ligands are replaced by H_2O ligands.

Finally, to understand the essential catalytic transformations involved in the conversion of glucose to fructose, electronic structure calculations were carried out to determine the potential surface of the conversion. From these results, we have demonstrated that Cr(III) has a unique capability of interaction with the enediol isomer of glucose and catalyzing hydride transfer to convert glucose to fructose. Both $CrCl_3$ and $CrCl_4$ were examined. The results provide the first potential surface and a detailed stepwise description of the catalytic conversion, revealing steps such as complexation with the enediol not available to copper and many other transition metals, but available to chromium. Extensive work was also carried out to determine how the skeleton of glucose evolves as it is converted to fructose and HMF using ^{13}C labeling methods. The labeling study uncovered the detailed pathway of conversion of glucose to fructose and the reverse conversion.

Thus, our work has brought glucose conversion to HMF to the point of being a practical industrial route to conversion of carbohydrate monomers to fuels. The work has demonstrated how molecular-level catalyst characterization can lead to successful catalysis-by-design. Similar work to enhance the fundamental catalytic steps of the copper/chromium catalysis of cellulose conversion to glucose are needed but will be carried out elsewhere.

Improved Selectivity for Explosives Detection by Ion Mobility Spectrometry

Robert G. Ewing, Melanie J. Waltman

◆ Detection of trace explosives is highly important to homeland security. Under this project, improvements to selectivity will greatly improve the utility of trace detection techniques. ◆

Trace detection is widely deployed as an explosives detection solution. Many airports rely on trace detection, typically ion mobility spectrometry, for aviation security. Although there are alternative techniques for detection, there are often deployment and operational issues with these systems, depending on the scenario. Because it detects the associated residue rather than the device itself, trace detection can be used in a wide variety of situations. Sensitivity and selectivity are the primary attributes that define trace detection performance. These attributes can be further delineated as probability of detection and false alarm rate. Although trace detection technology is fairly mature and heavily deployed, there are still significant opportunities for development. In spite of the high performance of the trace detectors themselves, enhancements to currently deployed instrumentation to increase sensitivity and reduce false positives are needed. New sensors under development must also demonstrate significant gains in performance in order to displace the current installed base of trace detection equipment in standard screening applications.

This research will be used to attempt to fill the selectivity technical gap mentioned above by providing additional spectral information through the generation of new ion species of explosives. These new ionic species will be created from a variety of reactant ions generated in both Ni-63 and corona discharge ionization sources. The new reactant ions may provide improvements to sensitivity as well, due to the suppression of chemical background noise. Another benefit of this research is in the use of a non-radioactive ionization source. There are several advantages including safety, environmental protection, and accountability when using non-radioactive ionization sources.

Neutral chemicals such as NO_2 and O_3 are known byproducts of operating a discharge source at atmospheric pressure. These neutrals, along with the O_2, N_2, and CO_2 already present and combined with an energetic electron, can yield a variety of ionic species, as shown in the reactions below. The probability of observing any one of these ions will depend on time and neutral vapor concentration and can be predicted by the given rate constants.

$e^- + O_2 + N_2 \rightarrow O_2^- + N_2 \qquad k = 1.0\text{x}10^{-31}\ \text{cm}^6/\text{s}$

$O_2^- + NO_2 \rightarrow NO_2^- + O_2 \qquad k = 2.0\text{x}10^{-9}\ \text{cm}^3/\text{s}$

$O_2^- + O_3 \rightarrow O_3^- + O_2 \qquad k = 6.0\text{x}10^{-10}\ \text{cm}^3/\text{s}$

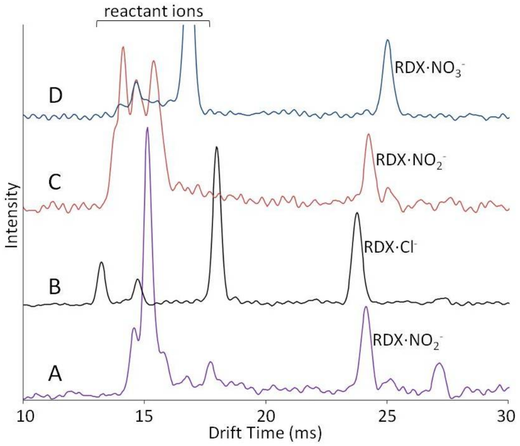
$O_3^- + NO_2 \rightarrow NO_2^- + O_3 \qquad k = 7.0\text{x}10^{-10}\ \text{cm}^3/\text{s}$

$O_3^- + CO_2 \rightarrow CO_3^- + O_2 \qquad k = 5.5\text{x}10^{-10}\ \text{cm}^3/\text{s}$

$CO_3^- + NO_2 \rightarrow NO_3^- + CO_2 \qquad k = 2.0\text{x}10^{-10}\ \text{cm}^3/\text{s}$

$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \qquad k = 1.2\text{x}10^{-10}\ \text{cm}^3/\text{s}$

Many explosives such as HMX, RDX, NG, PETN, and tetryl ionize via adduct formation with small anions available in the ionization region. The importance of this ionization mechanism is related to the ability to change anions that are available to interact with explosive molecules. We believe that we can take advantage of this ionization mechanism to improve both the selectivity and sensitivity of ion mobility spectrometry in detecting explosives. Various experiments were conducted to demonstrate proof-of-principle in the use of specific adduct ions to improve the selectivity of detection of specific types of explosive compounds, including RDX, PETN, nitroglycerine, tetryl, and TNT.



Ion mobility spectrometry of RDX with multiple reactant ions.

The end result of our research was a summary of mechanisms for explosive ionization occurring at atmospheric pressure with a variety of reactant ions. Understanding these mechanisms allows for predictive capabilities that can be applied to upcoming explosive threats and improved reliability of current detection technologies. Another outcome was a decision on the feasibility of using a non-radioactive ionization source with an ion mobility spectrometer, if such a source will provide different product ions and thus improve selectivity. The basic science aspects of this work resulted in several conference presentations and publications.

Instrumentation for Explosives Detection Research

Jay W. Grate, Norman C. Anheier Jr., Robert G. Ewing

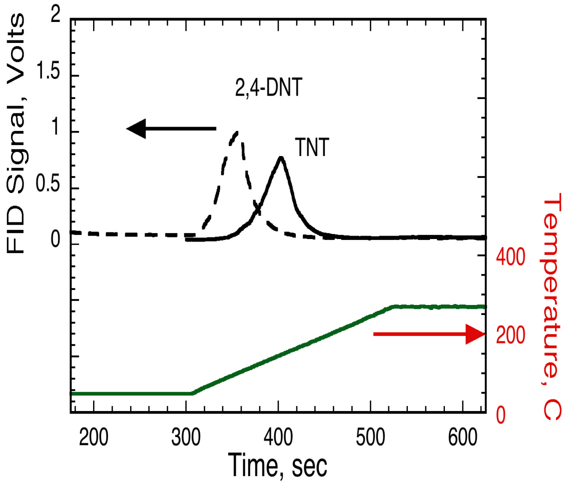
◆ Development of devices and instrumentation for explosives detection requires test and evaluation using samples of explosives molecules. This project has developed a new approach to the challenge of generating pulses of explosives vapors to enable research in explosives preconcentration, sensing, and detecting. ◆

Advanced sensors and instrumentation systems for trace explosives detection are required in environmental monitoring as well as national and homeland security. The detection of explosives is critical to security applications ranging from defense and homeland security applications to the protection of DOE infrastructure and assets. Detection of explosives vapors in the gas phase carried out using sensors or instruments is feasible; however, improvements are desirable. Development of advanced sensors and instrumentation requires a means to test and evaluate candidate devices and technology against explosives vapor samples. Explosives vapor generation systems in the literature generate vapors from neat solids, from materials adsorbed on inert solid supports, or from solutions containing explosives molecules. Most systems are custom built systems in the investigators laboratories to support their research.

Generation and delivery of explosives vapors is challenging for several reasons. Most explosive materials have very low vapor pressures. Hence, getting vapor molecules from a source explosive material into the gas phase in sufficient quantities and at sufficient rates is not trivial. Once generated, explosives vapor molecules tend to leave the gas phase by adsorption on tubing walls or other surfaces. Therefore, getting explosives vapor molecules from one place in the generator, transporting them to the outlet of the generator and finally to the device to be tested is complicated by losses to internal surfaces. Schemes are required to provide heating of surfaces as well as tubing, and where possible, sheath flows to keep the molecules away from surfaces. Finally, the explosives materials themselves are hazardous. For systems generating a continuous flow of vapor molecules, calibration is required, and the waste stream must be managed.

In this project, we worked on developing an explosives generator based on the injection of solutions of known volume containing a known mass concentration of explosives compound, deposition of the explosives molecules on a porous substrate, removal of the solvent by evaporation, and subsequent controlled thermal desorption of the explosive molecules from the surface of the porous medium into the gas phase. This instrument will be portable so that it can be moved from one laboratory to another in order to support various research projects.

Specifically, we developed a pulsed method of explosives vapor generation using a solution of the explosive in an organic solvent as the source. The solution is injected onto an inert metal material in a porous foam format, depositing a known mass of explosives compound while the solvent evaporates and is swept away. The porous metal foam is contained in a metal tube with integrated heating wires and thermocouple. A control system in hardware and software provides a method to heat the metal tube at preprogrammed rates. The explosives molecules are transferred from the metal foam to the gas phase by a programmed thermal desorption process upon heating the tube. Using heated transfer lines, the explosives molecules are transferred forward to a test apparatus.



Programmed thermal desorption of 2,4-DNT and TNT from the metal foam core in the explosives generation devices as detected with a flame ionization detector. TNT has a higher desorption temperature than 2,4-DNT.

To demonstrate this method, we set up a flame ionization detector (FID) downstream from the explosives pulse generator, connected by a short length of heated transfer tubing. The FID detected the solvent vapor passing through the system upon injection of the explosive-containing solution onto the metal foam. The FID also detected the explosives vapor upon programmed thermal desorption.

In further work, we are designing a complete system that will deliver the explosives vapor to test apparatus for the development of preconcentrators, sensors, and instruments for explosives detection.

Multiscale Investigation of CO_2 Behavior in Subsurface Under Extreme Conditions

Alexandre M. Tartakovsky, Andres Marquez, Guang Lin, Sebastien N. Kerisit, Andy L. Ward

◆ This project will address the fundamental challenge of understanding the properties and processes associated with complex and heterogeneous subsurface mineral assemblages comprising porous rock formations and the equally complex fluids that may reside in and flow through those formations. Specifically, we will focus on understanding the geochemical interactions of the caprock with ambient water and supercritical and dissolved CO_2. ◆

Sequestration of CO_2 in deep geologic reservoirs has proven to be a viable way for stabilizing global atmospheric concentrations of greenhouse gases, providing the time needed to transition from principally fossil fuel energy sources to renewable alternatives. Despite considerable research effort, little is known about chemical and physical interactions of CO_2 with water and mineral phases. At the same time, existing field scale models of CO_2 sequestration rely heavily on constitutive relationships that describe interactions of different solid and liquid phases in subsurface environments. Because these relationships are not grounded in first principles, the accuracy of constitutive relationships and field-scale models is difficult to estimate a priori. A comprehensive study of the complex coupling between sorption kinetics and CO_2/water composition, temperature, and pressure is difficult to conduct with laboratory experiments due to the extreme pressure and temperature conditions relevant to CO_2 sequestration. Pore-scale transport models proved to be a valuable tool for estimating the constitutive relationships for non-reactive, two phase flows and studying the effect of complex pore morphology on entrapment and dissolution of non aqueous phases.

Given these challenges, we propose to develop multiscale, multiphase flow and transport models to simulate a CO_2 behavior (flow and precipitation) in the caprock at both the pore and the subpore scales. This model will combine molecular dynamics simulations with lagrangian meshless solution of Navier Stokes and diffusion reaction equations. Molecular dynamic simulations alone are not able to cover sufficiently all of the length and time scales necessary and relevant to understanding the fundamental processes involved in CO_2 sequestration. The hybrid model will bridge molecular dynamics surface chemistry models and pore scale models and describe a complex behavior of the CO_2 subsurface in general and in the caprock, specifically. In addition, the hybrid model will serve as a basis for upscaling CO_2 behavior from the fundamental to one of practical importance.

To date, we have implemented an efficient atomistic scale approach, namely the kinetic Monte Carlo method, which allows for modeling the long time evolution of a particular atomistic system. We have applied this method to the simulation of CO_2/water mixtures in contact with calcite surfaces. The model can be used to describe the kinetics of calcite precipitation/dissolution as a function of temperature, pH, and CO_2/water composition. In particular, the model can account for the interplay between the effects of the decrease in pH and the decrease in calcite solubility as the CO_2 content increases. We have also developed a hybrid kinetic Monte Carlo diffusion equation method that couples the standard kinetic Monte Carlo model with a numerical solution of diffusion equation. This significantly extends the range of application of the kinetic Monte Carlo method by adding the bulk fluid diffusion.

Also during FY 2009, we developed a pore-scale smoothed particle dynamics model that simulates the dissolution of liquid CO_2 in water and the precipitation/dissolution of calcite. This model takes into account the changing pH of water and its effect on the dissolution and precipitation of different species. A Darcy scale fully Lagrangian particle model for flow and transport was developed and used to simulate gravity driven unstable flow of fluids with different densities. This model will be used to investigate the downward migration of dissolved CO_2. As the result of our research, one article has been published in *Computer Physics Communications*, and another manuscript is in progress.

Generally, we aim for the project to result in unique capabilities for understanding complex geochemical interactions of heterogeneous subsurface environment with fluid mixtures. Our primary outcome is highly scalable code able to model CO_2 behavior realistically at the interface and within the caprock at pressures and temperatures relevant to the geological CO_2 sequestration.

Throughout FY 2010, we will further enhance the code to create a database that can be used in advanced reservoir simulators that will include dissolution kinetics, solubilities and partitioning of different mineral phases. By the end of FY 2010, we will have developed the hybrid pore scale/ molecular dynamics model and further develop the molecular dynamics model for heterogeneous nucleation.

Multiscale Modeling from Molecular Reactions to Catalytic Reactors

Donghai Mei, Guang Lin, Alexandre M. Tartakovsky, Roger J. Rousseau, Michel Dupuis

◆ This project aims to develop a new modeling capability for reactor-scale catalytic processes informed by lower-scale simulations of chemical transformations on catalyst particles and molecular scale characterization of reactive processes at interfaces. ◆

A formidable challenge in catalysis research is to have a fundamental understanding of the mechanisms and dynamics of molecular transformations over catalyst materials under operating reaction conditions. Molecular-level understanding of catalytic reactions can enable one to design catalysts with improved efficiency (selectivity, yield, and cost) toward targeted products. However, operating conditions in reactors give rise to inhomogeneous temperature and pressure gradients experienced by the catalyst particles; a situation that dramatically complicates the macroscopic prediction of global kinetics and reaction yields. In this project, we are trying to develop a new computational module that describes heterogeneously catalyzed processes from quantum chemistry level up to reactor level under practical reaction and flow conditions.

Our approach includes the combination of theories and modeling at varied scales of length and time; that is, electronic structure theory (density functional theory and semiempirical of the same) for molecular surface reactions, stochastic reaction kinetics theory (kinetic Monte Carlo) for chemical transformations over catalyst nanoparticles, and mass, heat, and reactive transport theory (stochastic partial differential equation) for reactor models. The most challenging task in this unique computational module is the linkage of various theories and models at different time and length scales seamlessly and dynamically. We are trying to accomplish this linkage by modeling non uniform flow phase using both kinetic Monte Carlo and stochastic partial differential equation methods. As such, the two different methods are formulated in separate subdomains and are coupled via an overlapping region by communicating state information at the subdomain boundaries. The power of the new capabilities will be highlighted for specific catalytic systems by elucidating and predicting the catalytic transformations under practical reaction and flow conditions of a reactor.

During FY 2009, we developed a kinetic Monte Carlo simulation module coupling with three-dimensional grids describing the flow phase above the catalysts surface. In order to testing our new hybrid module, a benchmark catalytic system, carbon monoxide oxidation kinetics over rutile ruthenium oxide surface at varying temperature and gas phase composition conditions. This microscale model reaction information then was passed to a macroscale model in a form of a mass flux boundary condition.

Accurate implementation of the mass flux boundary condition presents a big challenge for grid-based macroscale numerical models, especially if boundaries are geometrically complex. We developed an improved numerical method for diffusion equations subject to Neumann or Robin boundary conditions. The Neumann and Robin boundary conditions are common to many physical problems (such as heat/mass transfer) and can prove challenging to implement in many numerical methods when boundary geometry is complex. The new method is based on the approximation of the sharp boundaries with diffused interface and the continuum surface force model and allows an efficient implementation of the Neumann and Robin boundary conditions. A manuscript describing this method was submitted to the *Journal of Computational Physics*. In addition, the model is used to simulate diffusion and surface reactions, and its accuracy is demonstrated through comparison with analytical and finite difference solutions.

During FY 2010, we will extend the method to treat the case of a non-uniform interfacial flow phase involving several catalyst particles and gas phase reactions in both the kinetic Monte Carlo and stochastic partial differential equation domains. The grid-based kinetic Monte Carlo model of the non-uniform interfacial phase domain will be involved not only in the coupling of the kinetics between the catalytic particles and the uniform main stream flow phase domain but also in the coupling of the reaction kinetics among the catalytic particles.

Our long-term goal is to develop a predictive, reliable tool for modeling catalytic processes in reactors from the determination of properties relevant to catalytic efficiency, such as overall reaction rates, product yields as a function of thermodynamic variables (such as the size, shape, and distribution of catalyst nanoparticles), composition of input reaction stream, and other operating parameters. Careful benchmarking of the newly developed computational tool for already extensively studied catalytic processes (i.e., water gas shift, methanol steam reforming) will be a critical task. The project will leverage computer science advances in solving stochastic partial differential equations, in unstructured meshing, and in massively parallel computing combined with large scale kinetic Monte Carlo simulations and fast density functional theory calculations.

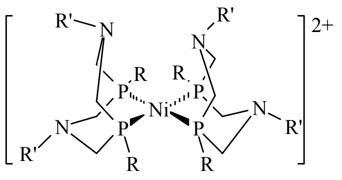
Ni-Based Molecular Electrocatalysts for Hydrogen Production/Oxidation

Daniel L. DuBois, James A. Franz

◆ Inexpensive molecular catalysts based on an abundant metal such as nickel for hydrogen oxidation may ultimately lead to viable replacements for expensive platinum catalysts currently used in hydrogen fuel cells. ◆

The development of fast, efficient, inexpensive catalysts for electrochemical production and the utilization of hydrogen will play important roles in developing the fuel cells and electrolyzers required for a hydrogen economy. The existence of hydrogenase enzymes based on Ni and Fe indicate that nonbiological catalysts for H_2 production can be developed. This project builds on previous research in which Ni complexes containing pendant N bases are catalysts for H_2 oxidation with low overpotentials. We probed specific structural features to develop inexpensive, air-stable catalysts with performance characteristics comparable or superior to those of hydrogenase enzymes. The enzyme characterizations have led to studies on simpler model complexes attempting to mimic the structure and function of these enzymes.

We previously reported the synthesis of a new series of Ni(II) diphosphine complexes that contain cyclic ligands of the general formula shown in the structure. In **1a**, $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$ serves as catalyst for the electrochemical oxidation of H_2 in acetonitrile solution in the presence of a base. In **1b**, the complex $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)](BF_4)_2$ is an effective catalyst for the electrochemical reduction of protons.



1a: R=cyclohexyl; R'=benzyl
1b: R=R'=phenyl
1c: R=cyclohexyl; R'=benzyl
1d: R=phenyl; R'=4-(thiophene-3-yl)phenyl
1e: R=phenyl; R'=4-(hexyl)phenyl
1f: R=phenyl; R'=$C_6H_4CH_2P(O)(OEt)_2$

An important question in the performance of catalysts is the role of the R and R' groups. When R=R'=phenyl, these complexes are catalysts for H_2 production. In FY 2009, we extended our studies to include new Ni complexes with R'=4-(thiophene-3-yl)phenyl (**1d**), 4-hexyl-phenyl (**1e**), and $C_6H_4CH_2P(O)(OEt)_2$ (**1f**). Studies of these complexes have shown that high catalytic rates are retained. These results bode well for further studies of this class of complexes.

Over the course of this project, systematic thermodynamic studies were carried out on complexes in **1a**-1**c** to determine the thermodynamic properties (shown in the table) of the corresponding hydrides of **1a**-1**c**. It is clear from free energies for heterolytic addition of H_2 to **1a-1c** that complex **1a** is biased by the nature of ligand substituents toward H_2 uptake. It is expected (and observed) to be the best of the three derivatives as a H_2 oxidation catalyst. Conversely, if this complex were to contribute to H_2 formation, the catalyst would be rapidly inhibited by the product unless H_2 could be continuously removed. Although the rates of H_2 oxidation and production in these catalytic reactions are controlled by transition state energies, a knowledge of factors controlling thermodynamics of the intermediates can greatly assist in understanding their bias toward H_2 production or oxidation.

Thermodynamic properties of 1a-1c and related complexes

Complex (RR')	$E_{1/2}$(II/I) for **1a-c**	$E_{1/2}$(I/0) for **1a-c**	pK_a (Ni-H)	ΔG°H- kcal/mol	ΔG°H• kcal/mol	pK_a (NH)	ΔG°(H_2) kcal/mol	E_{over}
1a (CyBz)	-0.80	-1.28	21.9 (23.0)	61.6 (62)	54.1	12.8	-3.1	0.1
1b (PhPh)	-0.84	-1.02	16.7 (17.6)	59.8 (61.3)	53.2	(6.6)	(+*7.1*)	0.4
1c (PhBz)	-0.94	-1.19	20.0 (21.1)	57.8 (59.5)	53.6	(12.8)	(+0.7)	0.1
PNP	-0.64	-1.24	22.2	66.7	53.2	10.6	-5.2	0.06
depp	-0.61	-1.34	23.3	67.2	54.4			

The observation that the potential of Ni(II/I) coupled for $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$ is more positive than the Ni(II/I) couples of $[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2](BF_4)_2$ and $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$ can be understood in terms of a larger tetrahedral distortion expected for $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$ arising from increased steric interactions between the cylohexyl substituents on phosphorus. This leads to the interesting situation in which a better electron donating cyclohexyl substituent results in a more positive Ni(II/I) potential, a better hydride acceptor, and a catalyst biased for H_2 oxidation compared to $[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2](BF_4)_2$, which has phenyl substituents on phosphorus that are poorer electron donors. These results indicate that the steric bulk of the phosphorus substituents can be used to tune the hydride acceptor ability of these complexes and bias the reactivity toward either H_2 production or H_2 oxidation if the pendant base is kept constant. Similarly, the electron-donating or withdrawing ability of the N substituent can be used to control the driving force for H_2 uptake or release, as seen by comparing $[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2](BF_4)_2$ and $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$. As a result, it is possible to tune the thermodynamic properties of these complexes for either H_2 production or oxidation.

Because proton relays may also play an important role in O_2 reduction catalysts, we extended our studies to include the reduction of O_2. This is another critical catalytic problem in the use of H_2 in fuel cells. To explore the role of proton relays in catalytic O_2 reduction, we studied the use of some of the complexes described above and found that they do have the ability to catalyze the reduction of O_2.

Oxygen Optode for Chemical Imaging in Microfluidic Microbial Models

Jay W. Grate, Marvin G. Warner, Norman C. Anheier Jr.

◆ Microorganisms that play crucial roles in nutrient, geochemical, and energy cycles on the earth do not act alone; rather, they perform as members of microbial communities. We are developing analytical methods based on fluorescent imaging (optodes) to observe oxygen concentrations within micromodels containing microorganisms. ◆

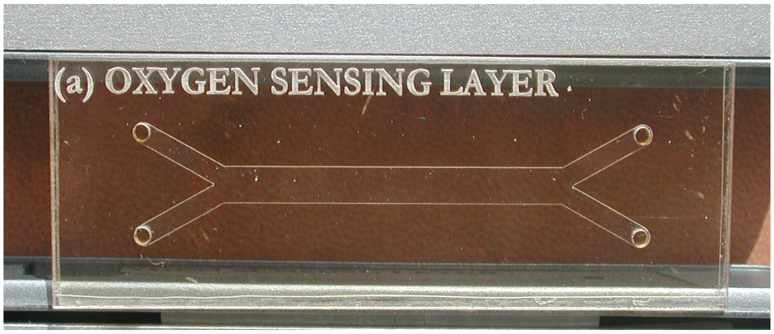
Microbial communities function in spatially heterogeneous microenvironments. Indeed, these communities contribute to the spatial heterogeneity by their growth and metabolism as well as by setting up local gradients. Understanding this heterogeneity as it relates to community structure, metabolism, and function is critical to understanding microbial communities. Planar optodes capable of chemical imaging in two dimensions represent a new approach to studying spatial heterogeneity in and models of microenvironments. Planar optodes consist of thin films that contain chemically sensitive fluorescent dyes. In combination with advances in optical imaging techniques and digital instrumentation, planar optodes extend prior work in fluorescent point sensors to two dimensions. In addition, they are compatible with recent advances in the development of microfluidic flow cells as models of heterogeneous environments at the submillimeter scale.

Key parameters for chemical mapping include oxygen, carbon dioxide, and pH. These materials each can be sensed optically using fluorescence measurements where the luminescence (or a ratio of luminescence features) is dependent on the parameter of interest. Devices to detect these analytes were originally developed as single point sensors, for example, by applying a polymer film containing a chemically sensitive fluorescent dye(s) to the end of an optical fiber. Fluorescent sensors for gases and electrolytes have also been developed as single particle or bead sensors. These fluorescence sensors are designed to be reversible, thus responding up and down to changes in the sensed parameter.

In this project, we are developing optodes to enable the imaging of oxygen concentrations across two-dimensional microfluidic models of porous media that contains microorganisms. We will focus on the development and implementation of oxygen sensitive optodes, as oxygen is a key parameter in many microbial systems. In addition, we are examining the process of measurement using intensities, fluorescence lifetimes, and ratiometric approaches. Oxygen imaging using a ratio of insensitive and sensitive luminescent peaks, rather than relying on more complex fluorescence lifetime measurements, will simplify measurement and implementation in microfluidic micromodels. Oxygen imaging will reveal the gradients within the porous structure of the micromodels and enable the observation of gradients that are associated with living biomass within the micromodel.

Development of this measurement capability requires several items of apparatus in addition to the fluorescent films. We have designed planar microfluidic flow cells with inputs for oxygen containing water and oxygen free water as well as the means of creating oxygen gradients. To deliver these solutions to the flow cell, we designed and obtained fluidic equipment. We have designed a gas mixing apparatus to generate dilute oxygen concentrations in the gas phase which will be used to equilibrate aqueous solutions to desired oxygen concentrations. In addition, we have designed optical measurement and imaging equipment that will allow us to examine fluorescent films in three distinct imaging modes: intensity, ratiometric, and lifetime.

We are also demonstrating oxygen imaging using dye containing polymer films within the gradient generating flow cells and further observe the effects of biomass on oxygen gradients. Specifically during FY 2010, we intend to develop the necessary composites and thin film layers for oxygen sensing, 2) complete assembly and system testing as well as assemble flow cells using the proper materials, 3) perform measurements with the optical imaging fibers, 4) demonstrate the oxygen imaging of a flow cell that contains microbes, 5) define the dyes and approaches for test platform integration, and 6) assess the extension to carbon dioxide and pH.



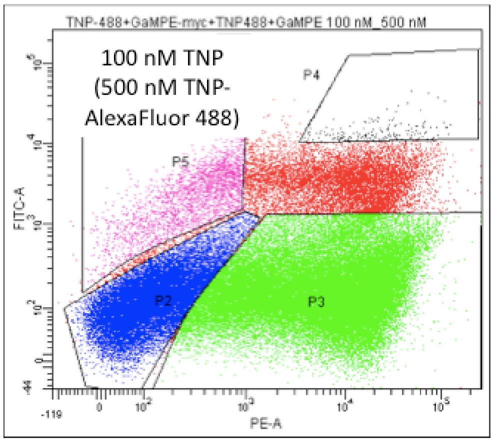
Simple two input microfluidic structure to test the ability of oxygen sensing fluorescent films under development to reveal oxygen gradients.

Reagent Selection Methodology for a Novel Explosives Detection Immunoassay Approach

Marvin G. Warner, Keith D. Miller, Cheryl L. Baird, Jay W. Grate

◆ The goal of this project is to develop methods for the identification and production of new biologically inspired reagents for the trace detection of explosives and their byproducts. This research will aid in the design and construction of next-generation detection systems capable of identifying trace levels of explosives in the field or laboratory setting. ◆

The detection of biological materials using antibody based immunoassays is a mainstay for biological and biomedical research, clinical diagnostics, biodetection, and food safety. Antibodies and fragments can be used to detect small (less than 1000 daltons) molecules such as those that comprise explosives. It has been demonstrated that synthetic antibody fragments could bind trinitrotoluene (TNT) selectively without displaying appreciable cross-reactivity with a variety of dinitrotoluene (DNT) analogs, thereby reinforcing the potential for high selectivity of these types of antibody-based reagents. The compatibility of protein-based reagents with harsh (by biological standards) extraction solvents (e.g., acetone) to solvate molecules effectively was also demonstrated. Immunoassays still face significant challenges with regard to obtaining reagents that yield specific and sensitive assays and from issues, such as nonspecific binding, signal interference (e.g., from scattered excitation light using fluorescent reporters), and sample matrix effects in homogeneous and heterogeneous immunoassay formats.



Flow cytometry dot plot shows the presence of TNT antibodies in a population of yeast specifically designed to express explosive antibodies on their surface. The yeast in region P4 is enriched in explosive specific proteins.

Open sandwich immunoassays have been described and are based on the induced dimerization of immunoglobulin G heavy and light chain domains in the presence of an antigen. The dimerized heavy and light chain subunits can be detected using either fluorescence or bioluminescence resonance energy transfer (FRET or BRET) pairs. In BRET assays, the Förster resonance energy transfer between a light emitting protein, such as luciferase and a fluorescence acceptor is measured as fluorescent emission at a different wavelength than the fluorescent protein alone. This method has a unique feature that no external excitation source is required to produce the fluorescence signal. BRET assays also have an advantage of addressing some shortcomings of traditional immunoassays (e.g., signal interference from scattered excitation light in fluorescent assays is no longer an issue of concern), so we focused efforts on using BRET- based immunoassays. The open sandwich assay format is in contrast to the standard sandwich immunoassay in that component subunits instead of intact antibodies are used, and the detection assay is based on antigen induced subunit dimerization. For example, in FRET and BRET formats, the target signal results from the fully assembled complex, not from individual labels. The open sandwich assay format can result in simple homogeneous assays or address problems such as background signals and nonspecific binding in heterogeneous assays. Nevertheless, developing a methodology to obtain specific antibody subunit pairs for open sandwich assays remains a significant challenge.

During FYs 2007 and 2008, we developed a high-throughput screening approach to identify antibody fragment pairs that dimerize only in the presence of antigen (i.e., RDX and TNT). In FY 2009, we investigated the production of scFv reagents and designed assays that employ them for detection of explosives and their byproducts. Specifically, we successfully produced antibodies with a high affinity and specificity toward TNT. As a result, we isolated effectively proteins capable of forming dAbs reagents and being employed in standard ELISA based assays for explosives.

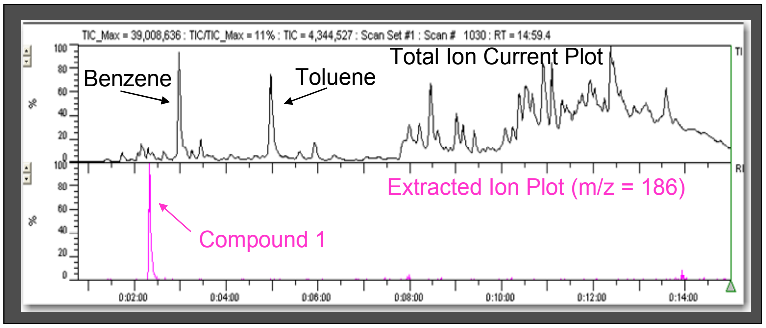
We rely on the expression of diverse variable heavy chain antibody fragments on the cell surface of yeast and the expression of diverse variable light chain fragments on bacteriophage surface. After incubation of yeast and phage display libraries with fluorescently labeled antigen, we use fluorescence activated cell sorting to select and characterize complexes that consist of yeast cells, phage particles, and fluorescent antigen. Our developed method is the first to use a high throughput system to produce reagent pairs for the open sandwich immunoassay technique with FRET or BRET detection. We also employed a quantum dot based BRET reagent using commercially available and synthesized quantum dots and *Renilla Luciferase* protein. Our methods for synthesizing the quantum dot, bioluminescent protein, and enzyme substrate (i.e., coelenterazine) that make up the BRET assay allowed us to explore interactions of these materials in parallel with protein reagent development.

Thermally Stable Chemical Markers

*Scott D. Harvey, Bob W. Wright, Norman C. Anheier Jr., Paula P. Bachelor, David A. Atkinson,
Robert G. Ewing, Timothy J. Johnson, Jon H. Wahl, Thomas S. Zemanian, Glen E. Fryxell*

◆ This project will define the best thermally stable fuel markers and characterize the throughput of the parent marker into the exhaust as well as define which characteristic signature markers are produced by combustion of the parent marker. ◆

Suitable fuel markers must meet a number of requirements: adequately soluble in fuel over a wide range of temperatures, thermally stable, sufficiently colorless and odorless to avoid easy detection by sight or smell, environmentally compatible, and easily detectable using analytical instrumentation. Molecular characteristics of thermally stable compounds include strong bonds and a rigid molecular backbone that can be conferred by an aromatic or polycyclic ring structure. Our studies will: 1) generate an initial marker list of less than 10 candidate compounds, 2) perform preliminary experimental oxidation studies (Phase 1) based on heating the sample in an inert quartz tube with air flow, 3) reduce the initial list to less than five compounds based on the degree of thermal decomposition observed in the preliminary oxidation studies, 4) test in a diesel engine (Phase 2) to obtain critical information on the marker recalcitrance and the identity and amounts of characteristic combustion products that are formed, and 5) prepare a final report that describes our findings.



GC/MS chromatograms of exhaust from a diesel engine burning fuel fortified with Compound 1. The top chromatogram is the total ion current chromatogram, where the bottom trace is an extracted ion current chromatogram that features an ion characteristic of Compound 1 (m/z of 186). This result shows that at least some of the parent compound survives combustion and is present in the exhaust.

During Phase 1 studies, an initial list of potential makers was investigated by oxidizing the compounds at 580°C in a quartz tube with air flow. The results showed little if any thermal degradation of the candidate compounds. These results are encouraging, but it must be acknowledged that oxidation in a quartz tube only crudely approximates combustion in an engine. Although the compounds were heated as rapidly as possible by sliding a preheated heater over the quartz tube, the heating was nowhere near as rapid as the millisecond cylinder transit time in an engine. Also, combustion in an engine exposes the compounds to high pressures, reactive intermediates, and catalytic surfaces that the Phase 1 studies could not simulate.

During Phase 2 studies, we examined the exhaust from a diesel engine burning fuel that contained potential marker compounds spiked, either individually or in combination, at about 100 ppm. The engine exhaust was analyzed by capillary gas chromatography/mass spectrometry (GC/MS). A trial examining fuel spiked with Compound 1 verified that at least some of the parent compound survived combustion and appeared in the exhaust. This finding was shown in the extracted ion current plot using a characteristic ion for Compound 1 ($m/z = 186$ amu). A retention time match with Compound 1 standards served to verify the identity of the compound. Similarly, we verified that Compound 2 was present in the exhaust from an engine burning Compound 2 fortified fuel. We currently are working out a mass balance to determine what fraction of the parent compounds survives combustion.

To investigate the presence of a specific marker breakdown combustion product, we analyzed the exhaust from a diesel engine burning higher concentrations of marker compounds (10,000 ppm Compound 1; 1,000 ppm Compound 2). For these experiments, analysis using Dräger colorimetric tubes determined that the concentration of the breakdown product in the exhaust was roughly 63 ppm. Theoretical calculations based on the engine operating parameters estimated that the maximum concentration of product would be 63 ppm, assuming complete conversion of the markers. The experimental measurements clearly indicate that a substantial conversion to the breakdown product occurs during the combustion process. Because GC/MS studies prove that some fraction of the parent marker compounds appear in the exhaust, we performed long-path infrared spectrometry on exhaust from an engine burning Compound 1 spiked fuel to determine the fraction of parent compound in the exhaust. This experiment indicated that less than 10 percent of the parent marker survived combustion.

We currently are performing a number of experiments to validate the mass balance for combustion of marker compounds. We also will be examining engine exhaust for a number of other markers that appear promising based on the results from the preliminary Phase 1 studies.

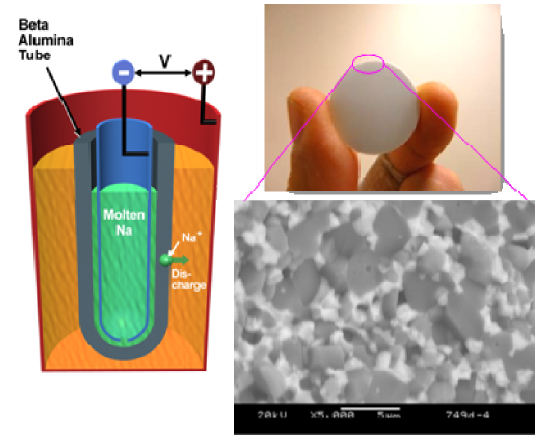
Transformational Materials for Advanced Stationary Electricity Storage

Z. Gary Yang, John P. Lemmon, Vincent L. Sprenkle, Gordon Xia, Daiwon Choi, Donghai Wang,
Xiaochuan Lu, Jianzhi Hu, Vijayakumar Murugesan, Vish V. Viswanathan

◆ To help design and develop cost-effective, high performance electrochemical energy storage devices or batteries, we will develop transformational materials and components. These efforts are enhanced by assistance from fundamental studies to obtain a mechanistic understanding of charge transport, electrode reactions, and interfacial properties in the electrochemical devices. ◆

Along with the current trend of carbon monetization, growing concerns for energy security and greenhouse gas emissions have spurred great interest in renewable energy from solar and wind. Effective utilization of the energy from these intermittent sources requires electrical energy storage, which can also improve the reliability and efficiency of the nation's electrical grid. The current electrical storage technologies, however, are not sufficiently mature in terms of performance nor are economically viable for the grid applications. A recent basic needs for electrical energy workshop clearly identified that significant breakthroughs in electrical energy storage technologies are needed to make intermittent renewable energy sources truly effective and to enable integration into the electrical grid.

Electrical energy storage can be realized either by direct storage in electrical charges or conversion of electrical energy into other forms of energy, among which may include chemical, potential, and kinetic. Direct storage technologies such as supercapacitors and superconductive magnetic electrical storage are highly efficient (close to 100 percent) but have low energy densities and discharge all stored energy in only seconds or sub seconds. Similarly, flywheels that store electricity via conversion into kinetic energy are capable of high power but much energy. Thus, these technologies are mainly used for power management instead of energy storage. The electrical storage in potential energy, such as pump hydro and compressed air storage may be appropriate for the gigawatt level of storage but unfortunately have geological and social/ecological limitations and require large initial capital investment.



A schematic of sodium beta alumina battery and a planar beta-alumina membrane, along with an enlarged electron-microscopic structure.

The technologies with the most viable options are the chemical storage or batteries, which are systems capable of efficiently storing electricity in chemicals and reversibly releasing it in accordance with the demand. Of particular interest for stationary electricity storage are sodium, redox flow cells, and lithium ion batteries. These electrochemical storage technologies can be potentially fabricated in modular systems capable of power/energy capacities ranging from kilowatt/kilowatt hours up to megawatt/megawatt hours, and discharging at the name plate power for durations of hours, both of which are critical to the renewable integration as well as grid applications.

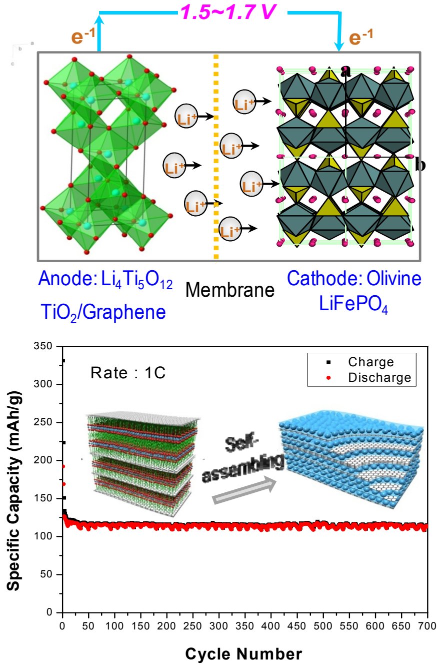
Stationary storage is an emerging area that has gained increasing interest among the research and industry communities. To strengthen PNNL's scientific capabilities in this critically important field, we propose to study and develop transformational materials for stationary electricity storage applications. By drawing on PNNL's synthesis and self-assembly capabilities, combined with our extensive solid oxide fuel cell and catalyst expertise, we can develop novel nano structures and architectures (and eventually new chemistries and catalysts) for electrodes and electrolytes used in advanced stationary battery applications. Thus, this project will build new PNNL capabilities that could enable the widespread adoption of renewable energy sources (wind and/or solar sources) in the science and technology of electricity storage for stationary applications. We expect to develop novel nanostructured materials and composites for next-generation of sodium beta, flow redox cells, and lithium ion batteries while obtaining the fundamental scientific knowledge necessary for successful development of advanced materials and advanced electricity storage systems.

Specifically, our project aims to develop each of the following:

- Novel solid electrolyte membranes with required sodium ion conductivity at intermediate temperatures (150 to 250°C) and cost-effective positive electrodes to construct revolutionary new sodium batteries based on planar, modular designs

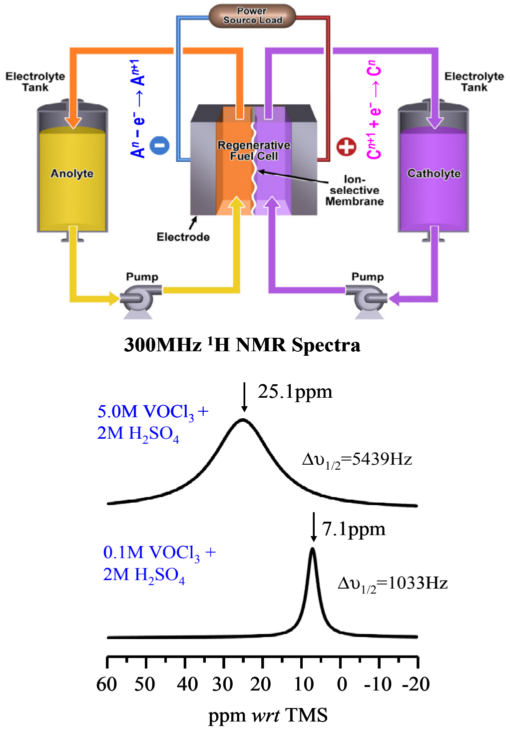
- Nanostructured electrodes of excellent structural stability and high lithium capacity for unique lithium ion batteries of long calendar/cycle life and low life cycle cost
- High energy solution electrolytes for redox flow batteries.

Sodium Beta Batteries. Our initial efforts have been on focused on developing novel oxide membrane of a satisfied sodium ion conductivity at temperatures below 280°C and cost-effective, optimized positive electrodes for new generation sodium beta batteries that are based on planar designs. A processing approach has been developed to make planar β" Al_2O_3 electrolyte that demonstrated satisfactory Na+ conductivity at the desired temperatures. The planar electrolyte fabricated was assembled into a planar cell that was successfully tested for proof-of-concept of the planar design.



A lithium ion battery for stationary applications; cell cycling performance of a battery cell made from self assembled composite electrodes.

Lithium Ion Batteries. For lithium ion community storage, the focus is on advanced electrodes made from TiO_2 base anodes and $LiFePO_4$ cathodes. Nanostructuring and composite approaches are employed to make the electrodes so that the unique lithium ion batteries can demonstrate a high rate capability, long calendar/cycle life, and reliability while being very cost-effective. For this long life, low cost battery type, we identified the TiO_2 base anode and $LiFePO_4$ cathode. We developed nanostructured composites of anatase TiO_2 and graphene as anode and $LiFePO_4$ cathode, and we carried out electrochemical and structural analysis on the anode/cathode materials. Additionally, we have assembled and cycle tested the TiO_2 base anode and $LiFePO_4$ cathode batteries for over 700 cycles with negligible degradation. We have carried out thermodynamic study that helps understand heat generation during electrochemical reactions.



A schematic of flow battery; nuclear magnetic resonance spectra of solution electrolytes.

Redox Flow Batteries. Regarding the flow batteries, the focus has been on study of chemistry and electrochemistry of all vanadium sulfate solution electrolyte. The basic study intends to obtain insights into the aqueous electrolytes and offer knowledge for optimization and modification of the chemicals. In particular, we carried out a nuclear magnetic resonance study on the all vanadium sulfuric acid base electrolyte at varied concentrations and temperatures. The work helped determine transport properties of active species in the electrolytes and mechanistically understand the charge transfer process.

Our project efforts thus far have produced the publication of four articles about our research in scientific journals plus two additional article submitted and two more in preparation. In FY 2010, we intend to continue nanocomposite work (synthesis, optimization, and characterization) for lithium ion batteries. Additionally, we will work to develop an understanding on battery reactions and transport during long-term cycling, commence developing sodium ion membrane electrolytes and halide cathodes, and if necessary, begin flow cell works.

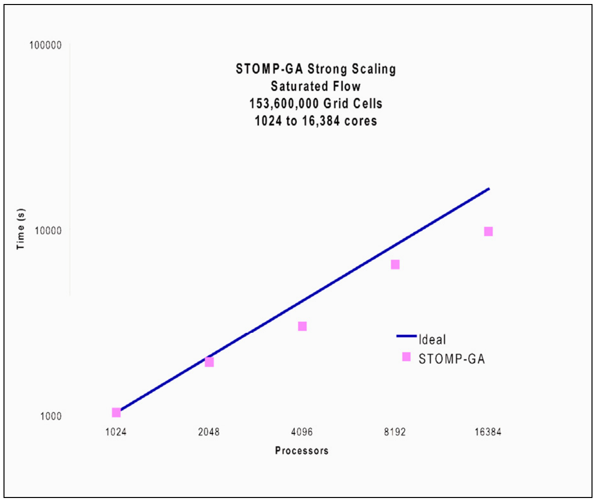
Earth and Space Sciences

Advanced Scalability for STOMP: Subsurface Simulation and Characterization at Extreme Resolution

Steven B. Yabusaki, Timothy D. Scheibe, Guang Lin

◆ Advanced computers and computational technology are enabling the development of more reliable predictions of the movement of fluids and contaminants in the subsurface environment. The subsurface simulation capabilities developed under this project will lead to reduction in risks to human health and the environment, and cost-effective solutions for waste cleanup, carbon sequestration, and hydrocarbon recovery. ◆

Reactive transport simulation codes have become widely used for simulating movement and fate of contaminants and other dissolved constituents in the subsurface. They are useful as engineering tools for site analysis and as fundamental research tools. While major advances have already been made in our ability numerically to simulate complex hydrologic, geochemical, and microbiological processes of interest, accurate and detailed characterization of spatial property distributions in the subsurface remains a primary challenge facing reactive transport modeling efforts. The extreme resolution targeted for computationally-based research on critical subsurface science issues requires highly scalable simulators that can fully exploit the high performance and large memory of advanced computers.



Strong scaling on the EMSL Chinook supercomputer for STOMP single phase flow through the 154 million grid cell domain.

Three broadly defined approaches were used to address incomplete subsurface characterization: inverse modeling, stochastic simulation, and hydrogeophysical interrogation. This research will draw on all three approaches in an integrated manner to develop and test a general approach to subsurface characterization and modeling with extremely high resolution of model parameters and processes. PNNL's Subsurface Transport Over Multiple Phases (STOMP) simulator is a state-of-the-art code used for all simulations of subsurface multifluid flow and reactive transport at the Hanford Site. A key component is reengineering the STOMP simulator to achieve a high degree of scalability on high performance computational platforms.

Profiling and scaling studies on existing STOMP code were performed, resulting in new software requirements for unstructured mesh support, boundary conditions, and time stepping. A new parallel processing version of the STOMP simulator that addresses variably saturated flow and multicomponent reactive transport was developed using the Global Array Toolkit, which supports a high level global shared memory programming style where the programmer is not responsible for process to process communication and does not require where data resides in distributed memory. A key finding is that our programming approach resulted in reuse of a large fraction of existing STOMP source code.

The new code was tested on up to 16,384 processor cores using the EMSL Chinook (HP DL185 nodes with 18,480 Opteron cores) and NERSC Franklin (Cray XT4 with 38,128 cores) computers. During testing, scaling bottlenecks were identified, and all bottlenecks in the STOMP calculation routines were subsequently removed; the only remaining impediments are associated with third party parallel libraries. Efficient strong scaling was demonstrated for single phase flow and transport up to 8192 processors. Application testing included the Hanford 300 Area uranium reactive transport and flow and transport through a highly resolved (156 million grid cell) depiction of braided stream channel deposits.

In FY 2010, we will test the range and robustness of the initial reengineered STOMP variably saturated flow and multicomponent reactive transport operational mode using large-scale, high-resolution applications; reengineer the STOMP CO_2 operational mode using Global Array and test parallel code with a geological carbon sequestration application for coupled multiphase fluid flow and geochemical interactions with highly resolved formation heterogeneities; implement routines and libraries supporting parallel I/O, load balancing, and visualization; and begin development of a large scale parameter estimation and uncertainty quantification capability for multiple simultaneous iterations/realizations using STOMP as the computational engine.

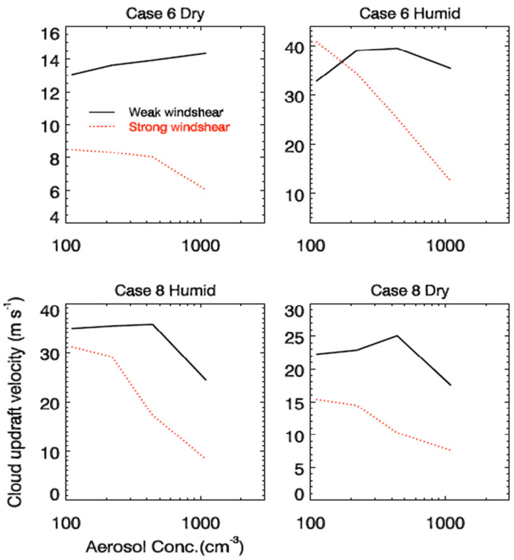
Cloud Resolving Model with Size Resolved Microphysics for Aerosol and Cloud Research

Mikhail Ovchinnikov, Jennifer M. Comstock, Sally A. McFarlane, Jiwen Fan

◆ One of the greatest uncertainties in projecting future climate comes from the difficulty in predicting the effects of aerosols on cloud formation. This project will build a cloud resolving model and evaluation tools that will improve our understanding of aerosol cloud interactions and aid in the development of improved parameterizations for global climate models. ◆

Aerosol's least certain and potentially strongest effect on the earth's climate comes from aerosol induced changes in cloud properties. Previously, some effort was applied to studies of aerosol effects on clouds, but few have integrated that knowledge into global models. Little effort has been applied to studies of aerosol effects on ice and mixed phase clouds. This project addresses these problems by integrating a detailed cloud microphysics model into the dynamical framework of a cloud resolving model, which is the primary workhorse of the multiscale modeling framework global model. The improved ice microphysics scheme allows us to simulate aerosol effects on Arctic stratiform clouds and deep convective clouds with higher fidelity. This model provides a consistent framework for testing and improving new parameterizations for climate models. In addition to model development, we also formulated a set of tools for model evaluation that simulate measured quantities using model output, which can then be compared directly with measurements.

In FY 2007, we collaborated with the Hebrew University of Jerusalem and a research group on merging their spectral bin model, which represents one on the most advanced available treatments of cloud processes, with a dynamical core of a cloud resolving model at PNNL. We performed initial test simulations on deep convective and Arctic stratocumulus clouds using the new model. In a parallel effort, we developed new model evaluation tools in the form of simulators of radar reflectivity and lidar attenuated backscatter, extinction, and depolarization ratio. The simulators can run either in line within the cloud resolving model or offline on model output and facilitate validation of model results with real observations.



Model simulations of several convective clouds show that aerosol induced changes in the convective intensity measured by the updraft velocity are a strong function of the vertical wind shear. Under strong wind shear conditions, increasing pollution always suppresses convection, most notably in a humid environment. Under weak wind shear, increasing aerosol concentration invigorates convection until it reaches a maximum at an optimal aerosol loading.

In FY 2008, we built model capabilities further, focusing on improving treatments of aerosol processes. Most importantly, a direct link between aerosol properties and ice nuclei (particles that lead to forming ice crystals in the atmosphere) has been established in the model. Ice nucleus size distribution has been added as a prognostic variable to the model, with ice nuclei sources and sinks explicitly calculated. The model was used to study ice formation and evolution in low level Arctic stratiform clouds.

During FY 2009, we further refined the model treatment of homogeneous ice nucleation at temperatures below –35°C. This process is critically important to the evolution of deep convective and cirrus clouds. Response of these clouds to changes in aerosol loading is not well-understood but is suspected to be climatically important. We systematically assessed aerosol effects on isolated, deep convective clouds based on cloud resolving model simulations with spectral bin cloud microphysics and analysis of satellite observational datasets. We found that a dominant role of vertical wind shear in regulating aerosol effects on isolated, deep convective clouds (i.e., vertical wind shear) qualitatively determines whether aerosols suppress or enhance convective strength. Increasing aerosols always suppress convection under strong wind shear and invigorates convection under weak wind shear until this effect saturates at an optimal aerosol loading. We also found that in a humid atmosphere, aerosols have the greatest potential to suppress convection when wind shear is strong.

Our findings reconcile some seemingly contradictory results of several past studies by considering the dominant effect of wind shear. Our results also provide insight to parameterize aerosol effects on convection by adding the factor of wind shear to the entrainment term, which could reduce uncertainties associated with aerosol effects on climate forcing.

The results from this project were presented at the American Geophysical Union annual meeting in December 2008 and are summarized in three papers: one published, one in press, and one in review.

Data Assimilation Tools for CO_2 Reservoir Model Development

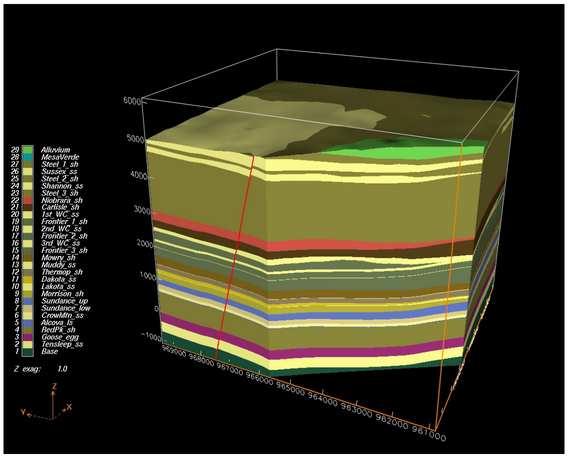
E. Charlotte Sullivan, Mark L. Rockhold, Christopher J. Murray, George V. Last, Gary D. Black

◆ We aim to develop improved, robust software tools and workflows for data analysis and assimilation tasks associated with the development and parameterization of subsurface reservoir models for CO_2 sequestration. Ultimately, our research results will help mitigate adverse effects of excessive CO_2 production on climate change by providing tools to facilitate modeling of subsurface injection for geologic sequestration of CO_2. ◆

Development and parameterization of conceptual and numerical models of large-scale subsurface reservoirs for CO_2 sequestration is a difficult, time-consuming process that requires the assimilation of multiple data types (core, borehole geophysical logs, seismic) representing different properties, processes, and scales of measurement. Development of large-scale reservoir models has generally been the purview of petroleum exploration and production companies. CO_2 sequestration involves additional processes such as geochemical reactions and buoyancy induced plume migration that must be considered in developing reservoir models.

The objective of this research is to build workflow and software tools that support data analysis and assimilation tasks for the development and parameterization of models of subsurface reservoirs for CO_2 sequestration. One of several collaborative research efforts, this project interfaces with a software development project that is developing a wiki based framework for organizing and tracking data and modeling results associated with numerical model simulations. This wiki based software framework and associated analysis tools are referred to as the Geologic Sequestration Software Suite, GS^3. Our project is assisting this other project with designing the layout of GS^3, providing recommendations on functionality and developing software tools for data analysis and assimilation that will be accessible from the wiki and facilitate building and parameterizing large-scale models of subsurface reservoirs. The GS^3 wiki and associated analysis tools are being demonstrated using application examples from real sites with active sequestration projects. A goal of the combined projects is to develop a software framework or platform and associated toolkits that streamline the process of reservoir model development and analysis.

During FY 2009, we interfaced with the software framework group to design the layout and recommend features/capabilities to incorporate into the GS^3 wiki. Specific suggestions include the following: linkage to MediaWiki application extension for GoogleMaps to display site features such as well locations; linkage to MediaWiki application extension for the open source plotting package GNUPlot; LAS file viewing and plotting for borehole geophysical log data; and linkage to R, an open source statistical analysis package that includes code for principal component and cluster analyses useful for facies delineation. In addition, we developed or linked to existing rock and fluid property databases.



Cutaway view of geologic units for a portion of the Teapot Dome Field in Wyoming generated using EarthVision™.

Also in FY 2009, we developed programs and scripts for tasks associated with data analysis and assimilation, some of which are used in the wiki: Petrl scripts for plotting borehole geophysical log data using GNUPlot; python scripts for converting public land survey system coordinates to latitude and longitude; Visual Basic programs for compositional analysis (determination of mineral volume fractions) from well log data; and Fortran90 programs for permeability and porosity upscaling. We compiled reference documents, generated an annotated bibliography, and initiated development of a rock properties catalog that will provide a source of generic and site specific physicochemical properties applicable to CO_2 sequestration modeling. Our work resulted in a technical paper and a presentation at the Geological Society of America annual meeting.

For FY 2010, we will continue developing technology and software, including data assimilation, preprocessing, and improvements to incorporating geochemistry into lithofacies and diagenetic facies definitions. We will fully define the conceptual data model and management tools to augment the strengths of existing software packages. We will develop tools that incorporate the strongest attributes of Petrel (or alternative software suite) with software currently being developed. Also, we will develop any needed database management tools and pre processing technologies.

Developing an Initial Framework for a Regional Earth System Model

Lai-Yung (Ruby) Leung

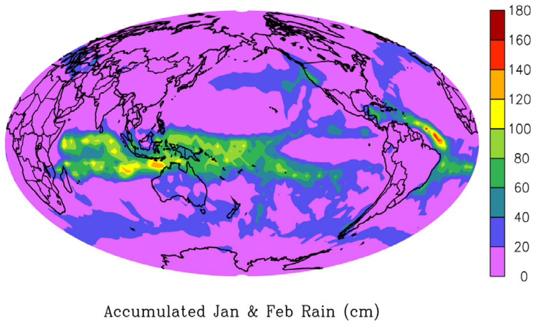
◆ We aim to implement a framework that will allow the weather research and forecasting model to adopt existing earth system components from the community climate system model through the flux coupler. ◆

Regional climate models have been used to understand regional climate processes and downscaling global climate simulations. Our objective is to develop a capability for weather research and forecasting to be coupled with earth system components from the community model to allow earth system processes and their interactions to be represented at the regional scale. We tested the coupling framework through weather research and forecasting with the Community Land Model—a vegetation atmosphere transfer model that simulates terrestrial ecosystems and soil moisture, runoff, and temperatures. Versions of the model include the carbon and biogeochemical cycles of carbon and nitrogen. We will adopt a complete model of terrestrial processes and the biogeochemical cycle that allows the regional model to study climate and land use change. We anticipate that advances in computing will enable the Community Land Model to be run at high resolution so that land surface heterogeneity in topography, vegetation, and land use can simulate land and water use effects and potential feedback. We will perform simulations using weather research and forecasting and Community Land Model applied to different grids and assess the impacts of Community Land Model resolution on simulating land surface processes.

In FY 2009, we developed an initial framework for a Regional Earth System model by pairing Weather Research and Forecasting and Community Land models using the community climate system model flux coupler. Through collaboration with the Naval Postgraduate School to develop the Regional Arctic Coupled model and the National Center for Atmospheric Research (NCAR), we obtained a version of weather research and forecasting coupled with Community Land Model and other earth system components of the Community Climate System model through the community climate system model flux coupler (CPL7). This modeling system includes code modifications to enable weather research and forecasting to interact with CPL7. With this setup (weather research and forecasting + community climate system), one can select to use the Community Atmosphere Model or weather research and forecasting as the atmospheric component, which can then be coupled to the land (Community Land Model), ocean (POP), and sea ice (CICE) models in the community climate system model. This framework allows one to use much higher resolutions using weather research and forecasting and regional domains to study climate change impacts on regional scales. It also allows for testing of parameterizations that are candidates for future high-resolution climate models using computationally cheaper regional domains.

PNNL is building the capability to understand the behavior of the coupled code and continue the software development. Progress towards the goal of a Regional Earth System model has progressed to the point of running the coupled Weather Research and Forecasting Community Land Model models on the local PNNL cluster for short test periods. Presently, the Weather Research and Forecasting and Community Climate System model code has several limitations. The first is that it works only on global grids due to limitations within the coupling framework. The second is that the model is not stable for long simulations. PNNL began working on the first problem in FY 2009. The issue associated with the coupling framework is related to the remapping and interpolation software (SCRIP) used to generate interpolation weights for remapping fields from one grid to another in spherical geometry. This issue is being addressed by the SCRIP developers at Los Alamos National Laboratory using regional grids that PNNL researchers developed for the United States as a whole and the western states at multiple grid resolutions. PNNL researchers are also developing input data needed to run the Community Land Model on high resolution regional domains.

Work on the second problem (model stability) has begun. The code has been successfully ported onto the NW-ICE cluster at PNNL, and we have familiarized ourselves with it and how it works. Our team has run the model on NW-ICE for a 3 month simulation, at which point it becomes unstable, similar to the Regional Arctic Coupled Model researchers' experience. This is most likely due to masking issues of land between the atmosphere and ocean components. The details of this problem are being investigated.



Accumulated precipitation for an arbitrary year simulated by the WRF model within CCSM framework. Coupled to WRF are the POP ocean, CLM land, and CSIM sea ice models. WRF grid spacing is 3 degrees.

Development and Evaluation of an Externally-Mixed Sectional Aerosol Model

Rahul A. Zaveri, Richard C. Easter, James C. Barnard;
Nicole Riemer, Matthew West (University of Illinois at Urbana-Champaign)

◆ Atmospheric aerosols (suspended, fine particulate matter) are widely recognized as key elements in many environmental issues ranging from global climate change and visibility to adverse effects on human health. To address DOE concerns about the safe production and use of energy, it is necessary to improve our understanding of the origin, fate, and properties of different types of particles commonly found in the atmosphere. ◆

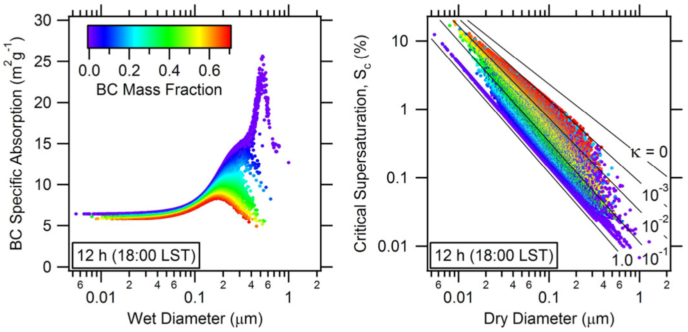
Atmospheric aerosols range from a few nanometers up to a few microns and can be composed of a wide variety of species, such as soluble salts, insoluble dust, soot, and organic compounds of anthropogenic and biogenic origins. Primary particles (i.e., emitted) and particles formed via homogeneous nucleation (e.g., sulfuric acid) are initially "externally mixed" (i.e., they exist as separate populations). Upon interacting with semi volatile gases in the atmosphere via condensation (and with other particles of similar or different compositions via coagulation), these particles undergo changes in size and chemical composition and gradually become "internally mixed" to varying degrees. This process is called evolution or "aging" of aerosols. The radiative properties, cloud condensation nuclei activation super saturations, and chemical reactivity of fresh and aged aerosol particles can differ significantly.

Accurately tracking the mixing state in conventional aerosol models requires treating a multidimensional size distribution, which is computationally prohibitive. Consequently, current aerosols models employ simplified treatments that may not adequately resolve aerosol mixing state. In this project, we use the newly developed particle-resolved aerosol model (MOSAIC-PartMC) as a numerical benchmark to guide the development of an accurate and efficient representation of the different particle types and mixing states in MOSAIC-ext to predict reliably the optical and cloud condensation nuclei activation properties.

The MOSAIC-PartMC model has been applied to an idealized urban plume case, in which pollutant trace gases and particles from diesel and gasoline engine exhaust and meat cooking were emitted for 12 hours into a well mixed urban air shed containing background aerosols composed of ammonium sulfate and aged organic aerosol. The urban emission profiles were based on Los Angeles emission inventory. Gas phase photochemical reactions and gas particle partitioning of various semi volatile species continued for 36 more hours in this urban air as it was advected away from the source region. By explicitly resolving more than 100,000 particles in a representative volume in this urban plume, the MOSAIC-PartMC model was able to simulate the evolution of the mixing state of urban soot particles as well as the associated optical and cloud condensation nuclei activation properties without any simplifying assumptions of particle mixing states.

The particle resolved results were reprocessed to analyze the numerical artifacts introduced into the predicted optical and cloud condensation nuclei activation properties due to the internal mixture assumption and the choice of bin size resolution commonly used in sectional aerosol models. We found that the optical properties are very sensitive to the aerosol mixing state, while cloud activation properties are more sensitive to bin size resolution and growth treatment than mixing state after the aerosol has photochemically aged for 4 to 6 hours. These and similar results for additional test scenarios will assist developing an efficient parameterization to account reliably for the effects of mixing states and bin resolution in a conventional sectional aerosol model. During FY 2009, we published two articles in peer reviewed journals, and another article is in preparation.

In FY 2010, we will focus on evaluating and improving the ability of MOSAIC-ext to represent ice nucleating properties of externally mixed aerosols as they age. The major issue related to ice nucleation aging includes the effects of condensation of inorganics and secondary organics as well as the effects of coagulation. Tasks include 1) extending MOSAIC-PartMC to handle coarse particles without substantially increasing the computational burden, 2) collaborating to develop test scenarios, performance metrics, and candidate formulations, and 3) running MOSAIC-PartMC to produce benchmark results.



Examples of optical and cloud activation properties of aerosol particles as a function of size and black carbon mixing state after 12 hours of photochemical aging. Each dot represents a particle.

Development of a Computational Fluid Dynamics Capability as a Tool for Exploring Atmospheric Processes

Julia E. Flaherty, Marshall C. Richmond

◆ Using computational fluid dynamics to investigate atmospheric processes provides detailed information about air flow and contaminant distribution that is not possible from field studies alone. The increased understanding of urban atmospheres will result in more efficient measures to protect citizens from daily pollutants and contaminants in industrial accidents or terrorist attacks. ◆

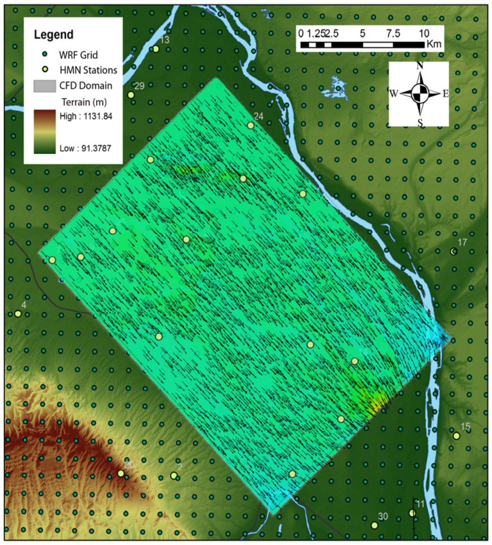
Urban computational fluid dynamics modeling as a research area has been growing in recent years in large part due to computational resource ready access. Once a modeling capability is established, a number of atmospheric science questions of interest to DOE could be explored using this modeling tool. Simulating outdoor urban air flows can guide more energy-efficient building designs, while turbulence modeling on wind turbines improves wind energy production. Technical achievement attained is the demonstration of high-resolution modeling as a tool for examining flows from urban to regional scales.

This project will develop computational fluid dynamics modeling capabilities for atmospheric processes with the goal of creating simplified guidance and tools for addressing the consequences of urban airborne contaminants. A number of recent urban atmospheric dispersion field studies provided an opportunity to study the real environment but are prohibitively expensive to conduct repeatedly. Leveraging the collected field data, computational fluid dynamics modeling systems can be used to conduct a systematic study of urban dispersion to provide empirical relationships between meteorology, urban morphology, and atmospheric dispersion. Using high resolution computational fluid dynamics modeling, basic guidance can be formulated to provide emergency response personnel with information needed to respond decisively and plan appropriately for an atmospheric release of hazardous materials.

During FY 2008, the commercially available STAR code was selected to conduct urban atmospheric simulations. Simple geometry cases such as a single box within a small computational domain were explored to gauge model performance characteristics and develop strategies for conducting the full city domain. Cases with simple geometries were examined to compare results with other codes. The STAR code was then exercised to determine that it has the utility to explore atmospheric processes at the scales in which our project was interested. The development of appropriate water-tight geometries and creation of a computational mesh suitable for atmospheric applications were also accomplished.

For FY 2009, the goal was to demonstrate a capability for tackling wind energy applications. To accomplish this, a steady-state case with k-epsilon turbulence closure was considered with boundary conditions developed from field measurements and boundary conditions developed based on results of running the weather research and forecasting mesoscale model. A major research gap in detailed computational fluid dynamics modeling is the uncertainty in the definition of these boundary conditions, and this work provides information on the limitations that result from imperfect boundary condition definitions.

First, a generic case with uniform inflow conditions was simulated as a demonstration of the proof of concept. Next, a simulation case was selected. Given the history of quality assured meteorological data available from the Hanford Site, we selected a domain that included a subset of the Hanford Meteorological Network. A period with fairly strong, steady winds was selected for the steady state simulation. For the first case, the four meteorological stations nearest the inflow boundary were used to develop a fairly simplistic set of profiles for the inflow condition. To contrast this, the second case was formulated from a plane of output data extracted from the weather research and forecasting simulation. The development of this modeling capability enables the ability to tackle difficult questions in atmospheric processes and provide solutions for needs nationwide.



Map showing the computational fluid dynamics domain with velocity field at 100 m above ground level. The simulation can be improved by defining inflow conditions from the dense weather research and forecasting grid compared with the less dense observation grid.

In Situ Imaging of Mineral-Supercritical CO_2 Reactions with Atomic Force Microscopy

A. Scott Lea, James E. Amonette; Steven R. Higgins (Wright State University)

◆ This project seeks to develop and demonstrate a novel, state-of-the art capability to investigate at the molecular-scale, the site-specific reactions that occur at the interfaces of minerals in conditions relevant to geosequestration in deep, underground aquifers. ◆

Storage of anthropogenic carbon dioxide (CO_2) in deep underground saline aquifers is viewed as a viable method to slow the increase of CO_2 in the earth's atmosphere while continuing to allow the use of fossil C-based fuels for energy. In these aquifers, CO_2 will exist in a supercritical (sc) state. Consequently, numerous bulk laboratory studies are underway to measure the thermodynamic and kinetic properties of the reactions that would occur for various mineral systems in the presence of hydrous, $scCO_2$. At the molecular-scale, site specific reactions occurring at these mineral fluid interfaces are entirely unknown. These fundamental reactions ultimately sum to produce the interfacial phenomena observed in bulk studies and described macroscopically by equilibrium thermodynamics or kinetic rate laws. An attempt to understand and control the chemistry at these interfaces, which is necessary to assess the practicality of subsurface carbon sequestration, should be based on explicit and quantitative understanding of these fundamental interactions.

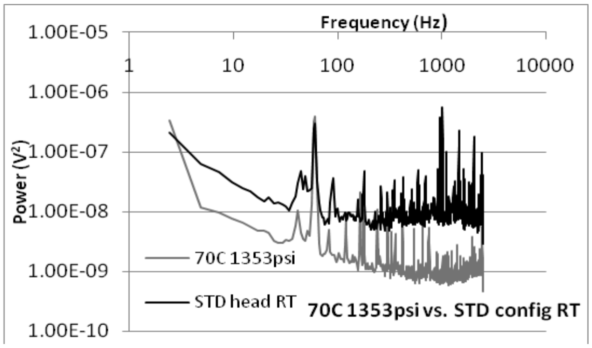
To address the above issues, we will design and build an atomic force microscope capable of operating at the high pressures and elevated temperatures that are expected to exist in these underground locations. This capability will be the first of its kind to be able to operate in both CO_2 and water dominant $scCO_2$ water phases where dehydration, mineral trapping, and solubility trapping reactions relevant to carbon sequestration occur. We will demonstrate the use of this newly developed capability to study the interfacial aspects of silicate dissolution and carbonation chemistry under supercritical conditions.

To date, we visited Wright State University for hands on experience with the hydrothermal atomic force microscope (AFM) in the laboratory, where, the test cell approach to development of the $scCO_2$ AFM was initiated. With the test cell, we can replicate conditions under which a cantilever will be interacting with a mineral surface in $scCO_2$ and make all critical noise measurements necessary to determine if the approach is feasible. In collaboration with the University and Lawrence Berkeley National Laboratory, we designed a fluid delivery system suitable for implementation with the $scCO_2$ AFM.

We designed and manufactured a high pressure test cell with a Digital Instruments Multimode AFM head modified to accommodate the test cell and eventually the $scCO_2$ AFM head. Connections are being made in the cell permit inlet and outlet ports for the $scCO_2$ and the introduction of a K-type thermocouple for the measurement of temperature within the test cell when noise measurements. Earlier calculations indicate that at 340 K and 80 bar, it is necessary to regulate the temperature to within the 0.1°C over a period of seconds to minutes to permit observation of atomic scale steps on calcite. Without this tight temperature regulation the systemic noise would be too large. We have been able to achieve this level of temperature control by placing the entire test cell and optical head inside a thermostatically controlled oven.

At 70°C and pressures up to 1353 psi, measurements were taken and compared with those measured with an AFM application head in its standard configuration. In its standard configuration, this AFM head has an rms noise level of 0.6 nm and is easily capable of resolving 3.2 Å atomic scale steps on calcite. With our $scCO_2$ charged test cell, we measured an rms noise level at half of what one sees with AFM in its standard configuration. These measurements the possibility of imaging atomic scale steps of calcite in $scCO_2$ with the $scCO_2$ AFM.

After successful AFM test cell design, we built the AFM head to incorporate into the machined head so that we will have a functioning unit. In FY 2010, we will demonstrate both mineral imaging and atomic resolution of mineral surfaces in $scCO_2$ and complete both anorthite and forsterite carbonation experiments.



Power density spectrum as a function of frequency for noise measured in the test cell at 70°C and 92 bar (gray) compared to the noise measured to an AFM head in its standard configuration (black) at RT and ambient pressures. The rms noise for the test cell is 3 mV, about half of the 6mV rms noise measured for the AFM head (~0.6 nm).

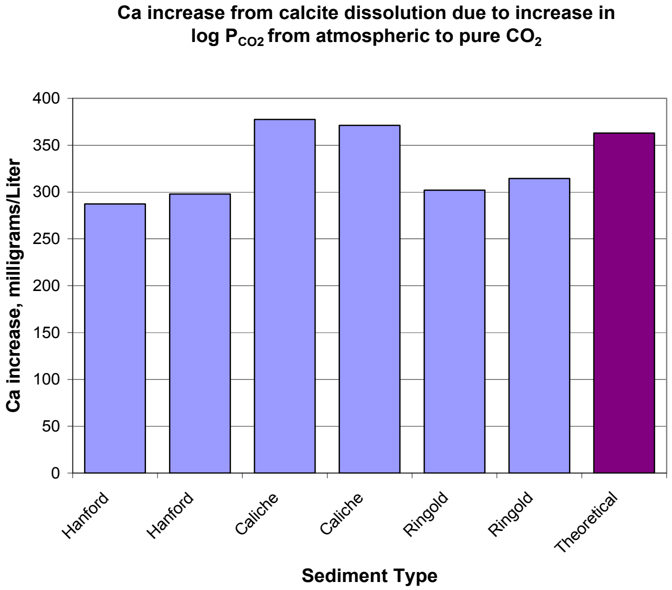
Manipulation of Carbonate Geochemistry for Sequestration of Contaminants

P. Evan Dresel, Nikolla P. Qafoku

◆ Remediation of contamination from the long-lived radioactive technetium-99 (Tc-99) is one of the greatest challenges in cleanup of the U.S. Department of Energy's nuclear facilities. We investigated a method for dissolving and reprecipitating natural carbonate minerals to coat and immobilize Tc-99 and other contaminants in the environment. ◆

We aim to develop methods for manipulating the in situ formation of carbonate minerals for physical incorporation of Tc-99. This work will focus on the formation of calcium carbonate minerals calcite/aragonite/vatterite and the ferrous iron carbonate siderite. Calcium carbonate is ubiquitous in the Hanford vadose zone and thus is a good target for dissolution/reprecipitation to form mineral overgrowths. Siderite formation likely will simultaneously reduce Tc(VII) to Tc(IV) during precipitation but adds the complexity of maintaining Fe(II) in solution until it reacts at the target zone. This project will produce a method for remediation of Tc-99 in the deep vadose zone, ready for testing at intermediate scale for development of a field demonstration. This fills a gap in the overall remediation strategy for the deep vadose zone. Ancillary benefits will include the potential to extend the methodology to other contaminants such as uranium, which is also readily reoxidized, and a better understanding of the complex interactions controlling subsurface carbonate mineral dissolution and formation.

Adding CO_2 gas to groundwater or soil pore water produces carbonic acid, which dissolves carbonate minerals. Shutting off the CO_2 supply and allowing the solution to degas can cause the minerals to reprecipitate. During this process, dissolved Tc-99 can be captured by reduction reactions and either precipitation in the carbonate mineral structure or by adsorption onto mineral surfaces that then are coated with the precipitated carbonate minerals. We used chromate as a substitute for the radioactive Tc-99 to evaluate the ability to fix the contaminants in place so that radioactive controls were not required.


Ca increase from calcite dissolution due to increase in log P_{CO2} from atmospheric to pure CO_2

Previous studies attempting to fix Tc-99 in place through chemical reduction have found that it is rapidly reoxidized and remobilized rather than being permanently sequestered. Our approach complemented these studies by providing a physical-chemical mechanism to remediate the subsurface contamination. Carbonate minerals, particularly calcite (calcium carbonate), are ubiquitous at many sites and their solubility is sensitive to pH changes, making them candidates for mineralogical sequestration.

Our experiments manipulated carbonate stability by varying the amount of CO_2 from natural air to nearly pure CO_2 and then shutting off the supply to allow the system to return to equilibrium with air. We performed experiments with three representative sediments—i.e., Hanford formation, Ringold Formation, and caliche layer—which had different calcite abundances. Another set of experiments were conducted with these three sediments amended with siderite (ferrous iron carbonate). Iron carbonate provides simultaneous reduction of the chromate by ferrous iron and carbonate mineral for sequestration.

We monitored the progress of carbonate dissolution/reprecipitation by monitoring the pH change in the reaction vessel and through chemical analysis. The results agreed well with theoretical models, demonstrating the ability to manipulate the mineral systems as shown in the figure. Slightly less calcium increase was seen in Hanford and Ringold formation sediments compared to the caliche layer, likely due to competing dissolution or ion exchange reactions.

Little chromate was removed using calcite alone, indicating the need to supply a reductant during remediation. Up to 90 percent of the chromate was removed by amending the sediments with siderite as a reductant even though siderite solubility is lower than that of calcite. Ferrous iron can reduce Tc-99, but previous studies have shown that it will re-oxidize with time and become mobile again. Our experiments indicate that coupling Tc-99 reduction by ferrous iron with precipitation of siderite or calcite is a viable concept for permanent immobilization although further steps are needed to design and test a subsurface remediation system.

The Aerosol Modeling Testbed

Jerome D. Fast, William I. Gustafson Jr., Elaine G. Chapman, Richard C. Easter, Jeremy P. Rishel

◆ Our streamlined modeling paradigm systematically and objectively evaluates aerosol process modules, better quantifies uncertainties by targeting specific processes, provides tools that facilitate science by minimizing redundant tasks, documents performance and computational expense over time, and fosters international collaboration among aerosol modelers. ◆

As reflected by reports from the Intergovernmental Panel on Climate Change, the consensus of the scientific community is that the direct (scattering and absorption of radiation) and indirect (cloud-aerosol interaction) effects of aerosols predicted by global climate models still contain large uncertainties. Therefore, we have developed an Aerosol Modeling Testbed (AMT) to understand uncertainties associated with specific aerosol processes over a wide range of spatial and temporal scales before new algorithms are implemented in global climate models. The AMT consists of a fully-coupled meteorology-chemistry-aerosol model and a suite of tools to evaluate the performance of aerosol process modules via comparison with a wide range of field measurements.

The research consisted of four tasks: 1) increasing the modularity of aerosol process modules within the chemistry version of the Weather Research and Forecasting community model (WRF-Chem), 2) developing the AMT based on a systematic evaluation methodology through testbed cases and software called the Analysis Toolkit that extracts and compares the model results to field measurements, 3) porting the AMT to multiple computational platforms, 4) and testing new aerosol treatments from other investigators through the AMT framework.

The first testbed case that uses the meteorological, chemical, and particulate measurements collected during the March 2006 Megacity Initiative: Local and Global Research Observations (MILAGRO) field campaign in central Mexico was completed. The resulting unified dataset, containing over 21,000 files and is 61 Gb in size, brought together information from several archives into one common format to ease its use for modeling. From this, "cloudy-sky" testbed cases that focused on cloud-aerosol interactions were initiated by processing data from the 2007 CHAPS and 2008 VOCALS field campaigns data into the AMT format.

The modularity of WRF-Chem was improved by developing a consistent methodology for treating aerosol optical properties, aerosol-radiation-cloud interactions, and dry deposition. The Analysis Toolkit was created, a suite of tools that extracts model output to mimic data obtained from surface, aircraft, vertically pointing lidar, and satellites using "instrument simulators." Graphical and statistical tools based on Gnuplot freeware for platform compatibility were designed to provide users "quick-look" plots and performance metrics. Portability and scaling tests of WRF-Chem were performed on EMSL's Chinook and NW-ICE high-performance computer clusters. Asynchronous I/O greatly reduced time spent writing output files using hundreds of processors. We found that the default settings on Lustre-based file systems slowed AMT, but tuning the settings significantly speed up its operation.

To demonstrate the capabilities of the AMT, we compared the performance of two aerosols models, Modal Aerosol Dynamics Model for Europe (MADE)/Secondary Organic Aerosol Model (SORGAM) and Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), within WRF-Chem. MADE/SORGAM employs a modal approach to represent the aerosol size distribution and an equilibrium treatment for gas-to-particle partitioning. MOSAIC employs a sectional approach for the aerosol size distribution and a dynamic treatment for gas-to-particle partitioning. MOSAIC is theoretically more complex and computationally more expensive than MADE/SORGAM; therefore, comparing the models within the AMT would determine whether the change in performance is worth the additional computational expense. Even though MOSAIC has 2.7 times as many species as MADE/SORGAM, it is only 1.8 times more computationally expensive. As part of our systematic evaluation methodology, all other processes (emissions, meteorology, photochemistry, boundary conditions, aerosol-radiation-cloud interactions, and dry deposition) employ the same treatments. In this study, treatments for secondary organic aerosol formation were turned off in both models.

A total of 24-day simulations for the MILAGRO testbed case were performed for both aerosol models and evaluated using the Analysis Toolkit. We found that close to Mexico City, both models produced similar aerosol mass and composition both at surface sites and along aircraft flight paths. While some statistics for MOSAIC were somewhat better than MADE/SORGAM and vice versa, neither model out-performed the other over the central Mexican plateau. However, differences in aerosol mass between the two models were produced further downwind along the coast and over the Gulf of Mexico. Nitrate and aerosol water were the species that contributed to most of the differences in aerosol mass. These differences can be attributed to differences in the equilibrium and dynamic gas-to-particle partitioning treatments. Nitrate predicted by MOSAIC was higher than MADE/SORGAM and significantly closer to aircraft measurements in this region. Aerosol water from MOSAIC was also higher than MADE/SORGAM, but there were no measurements to verify which model was closer to reality. Other aerosol species such as sulfate, ammonium, organic matter, and black carbon were within a few percent of one another, and these small differences can be explained by how the same treatment of dry deposition behaves for modal and sectional aerosol size distributions. Sensitivity tests that turned dry deposition off showed that both models produced the same organic matter and black carbon mass given the same emissions and meteorology, thus demonstrating how the AMT methodology can be used to target individual aerosol processes.

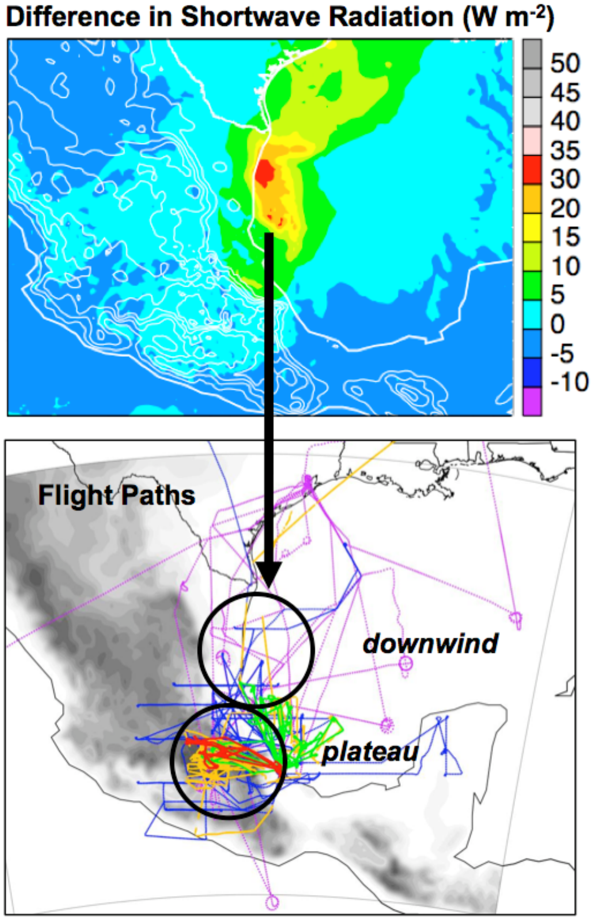
To investigate how differences in aerosol mass and composition affect radiative forcing, simulated aerosol optical depth (AOD) was compared against ground, satellite, and aircraft lidar instrumentation. Since both models produced similar aerosol mass and composition near Mexico City, not surprisingly the AOD was similar in that region. Spatial distributions of AOD revealed larger difference between the two models along the coast and over the Gulf of Mexico that corresponded to differences in aerosol mass and composition. It is important to consider that satellite measurements have large uncertainties over land and showed unphysical gradients near the coast. While both models produced high AOD along the coastal plain where higher relative humidity increases aerosol water and scattering, satellite data indicated a sharp drop in AOD from the ocean to land. Aircraft lidar sampling across the coast, however, showed no such gradient. The spatial variations from both models were consistent with lidar data in the region. MOSAIC tended to produce better profiles of extinction over the ocean, suggesting that sea-salt and aerosol water were better represented.

Differences in the predicted aerosols between the two models also affected the regional distribution of surface shortwave radiation. Nitrate and aerosol water were the primary reasons for differences in shortwave radiation, although differences in the aerosol size distribution via dry deposition also played a secondary role. Interestingly, the largest differences occur where relatively few aircraft missions were conducted. When the MILAGRO campaign was organized, sampling the evolving Mexico City pollutant plume as it was transported into the regional environment was the primary objective. Model results such as these were not available to contribute the scientific objectives of the program. The differences between aerosol models generated by the AMT could be used in the future to guide aircraft operations so that sufficient information is collected where the largest uncertainties among models occur so that treatments for specific aerosol processes can be improved.

Given that MOSAIC is approximately twice more computationally expense than MADE/SORGAM, the benefits of MOSAIC are more apparent at the regional scale. For local-scale simulations, the simpler MADE/SORGAM may be sufficient. Our results also demonstrate that it would be useful to have a version of MOSAIC than employs a modal representation of the aerosol size distribution, which would combine the advantages of both models. Already presented at several conferences, a description of the AMT and results comparing MOSAIC and MADE/SORGAM are currently being written as a journal article.

A portion of the code developed for the AMT was adopted by the WRF Atmospheric Chemistry Working Group and included in version 3.1.1 released to the community in June 2009, successfully demonstrating the concept of distributing improved techniques to other scientists.

The AMT is designed to foster collaborations between PNNL staff and the aerosol scientific community and extend PNNL's capabilities in regional-scale aerosol modeling. We are already collaborating with several "beta" users that are testing the Analysis Toolkit as part of their research.



Difference (MADE/SORGAM –MOSAIC) in shortwave radiation (top) at 19 UTC March 19, 2006 in relation to aircraft flight paths during the MILAGRO field campaign (bottom).

Transfer and Evaluation of the Community Atmosphere Model Parameterization Suite to Weather Research and Forecasting Model

Philip J. Rasch, Jerome D. Fast, Steven J. Ghan

◆ We will provide an opportunity for comparing the treatments for processes used in global climate models with those commonly used in cloud/mesoscale models and enable a systematic, consistent methodology to evaluate various treatments of physics, chemistry, and feedback processes for both types of models that will help improve both model classes. ◆

Global climate models are tools used to represent a comprehensive statement of interactions between complex processes that govern evolution of the earth's climate and assist science and society in understanding and projecting climate change. Although they try to be comprehensive, they are by nature incomplete, imperfect, and require many approximations to make calculation affordable. For example, global climate models predict features of the atmosphere at large spatial, temporal scales to reduce the calculations required to project climate, but multiple features (like cloud systems) must then be treated with complex approximations (parameterized) because they operate at scales below those resolved by the model. Regional models and those resolving features down to a single cloud system can utilize fewer approximations and may be conceptually simpler because fewer features occur at the sub-grid scale. They can also use more complex, elaborate representations for processes because they simulate features for shorter time scales over smaller regions. Historically, they have been too costly to be run globally for periods of climatic relevance. Thus, two communities have evolved that view the world differently and focus on unique methods. As science has evolved, these communities' interests have gradually intersected, but the tools (models) used make it challenging for one community to exploit the strengths of the other.

The aim of this project is to explore the integration of a suite of physical parameterizations (radiative transfer, convection, turbulent boundary layer, aerosols, cloud microphysics) from the Community Atmospheric Model (CAM) in the Weather Research and Forecasting (WRF) model and produce an initial evaluation of this suite of parameterizations in WRF. This exercise will provide an opportunity for comparing the parameterizations commonly used in cloud/mesoscale models with those in global climate models and provide a means of quantifying the performance of new process modules before they are incorporated into and used by global climate models. The merger will produce a synergy in modeling activities for weather and climate.

Configured as an aerosol modeling testbed at relatively high spatial resolution, WRF facilitates comparison to field measurements. By adding the suite of physical representations from CAM to WRF, we can help separate sensitivity of solutions to spatial resolution from changes in process representation. This provides a useful tool to aid community climate system model simulations by assessing the performance of aerosol-cloud-radiation interactions, where they can be evaluated at regional scales more appropriate for atmospheric radiation and science field measurements. WRF could also be run at two types of resolution: the local/regional scale appropriate to comparison with measurements and synoptic scale more consistent with typical resolutions used in global models. In this way, WRF assesses scale dependency of CAM physics schemes so that we know how they perform at higher resolutions. Some CAM physics may be inappropriate at regional scales, and global simulations at such fine scales would be cost prohibitive.

During FY 2009, the version of the CAM physical parameterization suite that we wished to use remained in development and behind schedule. As an alternative, we started the project using a current model that will be close to the final version in terms of software structure. Thus far, we have ported the model to PNNL computer systems and installed the software useful to understanding and interpreting results. We contributed to completing parameterization development of CAM by modifying the suite and diagnosing model simulations. To make sure our efforts are recognized and embraced by the broader scientific community, we continued discussions regarding software engineering strategies and goals with the relevant National Center for Atmospheric Research communities (Climate and Global Dynamics for CAM; Meso and Microscale Meteorology for WRF). While completion of the final parameterization suite is uncertain, significant progress has been made. The suite is producing a reasonable response to aerosol forcing and credible coupled simulations, which was not the case 4 months ago.

For FY 2010, we have scheduled the following tasks: port CAM physics into the WRF, check that the new code is WRF-Chem code compliant, verify the interoperability of CAM physics and existing chemistry options, confirm whether WRF driven by boundary conditions from CAM can reproduce the same biases, conduct a case study, produce a journal article on strategy and case study findings, and present at the CAM and WRF workshops.

Understanding Adaptation to Sudden Climate Change Impacts

Anthony C. Janetos, Hugh M. Pitcher, Allison M. Thomson

◆ The importance of rapid, unexpected change in the environment is cause for concern, though whether it is the fault of floods, pests and disease, or drought is not well understood. This research will explore the fundamental reason why such modifications occur in natural resources and how we may respond to it. ◆

Climate impacts have received attention in domestic and international scientific literature. Adaptation has been the focus of intense interest in the buildup to the Copenhagen meeting on a replacement treaty for Kyoto. Ecosystem and natural resource effects from climate variability and change are also being documented, and worldwide adaptation measures are being suggested or implemented. These observations present challenges to modeling frameworks used in integrated assessment. To be complete, models need to represent consequences of climate change and proposed measures to manage the changes.

The aims of this project are to develop the analytical engine for impacts in the integrated assessment models and an analytical framework for extreme or sudden events. We are conducting data analysis, model development, and ultimately model testing and evaluation. Several years ago, there was concern for the climate impact from a potential sharp reduction in the strength of the Gulf Stream or large scale emissions from methane hydrates. In a recent report on abrupt climate change, these risks are considered to be minor, which leaves tipping points or crossing thresholds that cause major change in system behavior and events such as heat waves or droughts as potential causes for sudden climate change impacts.

Research in FY 2009 focused on accessing and analyzing large numbers of climate scenarios and examining an example of adaptation to a threshold event driven process. We developed a prototype tool that can convert climate data to a set of anomalies from the base period, combine this with the University of East Anglia's base period climatology to develop estimates of temperature, select a U.S. or Canadian region, and develop area and population weighted estimates of temperature, heating degree days and cooling degree days both nationally and by base period temperature bands.

The prototype was exercised on 16 monthly temperature realizations from a 2004-2005 climate model completed for the Intergovernmental Panel on Climate Change. Realizations each for the following cases were examined: commitment, assuming concentrations of greenhouse gases were held fixed at 1999 levels of 360 ppm for CO_2 and three scenarios from the panel's special emissions scenario report. Examination of the model runs suggests that 1) for the period through 2040, there are only minor differences in future warming across the three future scenarios, 2) warming will increase by a factor of two (or more) as one moves from south to north within the United States, and 3) variation in temperature will result in the appearance of cooling even for the 15-year periods. The insensitivity of the climate results to changes in near-term emissions arises because climate is a function of the stock of greenhouse gases in the atmosphere, which is 100 times larger than current emissions. Mitigation can have only minor effects in the near-term but is vital to create better options in the future. The prototype is currently being examined for its suitability for serving as the basis for adding the ability to analyze the impact of changes in heating and cooling degree days on building energy use.

The relisting of the grizzly bear from devastation of the white bark pine tree caused by pine bark beetles yielded an examination of Yellowstone weather data. Since 1991, winter minimum temperatures have increased by 20°F, roughly a 6000-foot increase in the altitude at which it gets cold enough to provide control over the beetle. This assumes a 6.5°C per km lapse rate and –35 as the killing temperature, explaining why the pine is in danger. With an increase in summer temperatures that shortens the beetle life cycle, drying that increases the vulnerability of trees to infestation, and a forest heavily populated with older trees due to fire suppression, it is easy to see why there is a problem with the beetles and why the loss of the white bark pine has been so widespread. Intervention is not feasible, and the potential natural system adaptation is not currently known.

Adaptation for heat wave mortality occurs today, with much lower levels of mortality seen in the south, presumably from the widespread availability of air conditioning. Rapidly penetrating housing, air conditioning approached saturation in only the hottest parts of the country in 1985. By 2005, all parts of the United States with more than 1200 cooling degree days were saturated. As climate warms, private sector adaptation in the form of increased air conditioning use or changes in building design will replace the need for public sector programs. Ongoing work with the University of Maryland suggests that air conditioning offsets impact of heat waves when penetration is complete.

It is obviously important to extend the tool to access other variables and work with daily data. Though monthly files take about a half gigabyte per variable per realization, daily data runs about 30 times larger but will be important to understand the potential for major heat waves. Ultimately, what will matter is a deeper understanding of variability. Based on near-term insensitivity to climate emission, there is a need to rethink how scenarios should be developed and used in adaptation work.

Energy Supply and Use

A Real-Time Optical Spectroscopy Platform for Investigating Molecular Mineral Transformations for CO_2 Storage

Zheming Wang, Christopher J. Thompson, Alan G. Joly

◆ In situ investigation of the molecular mineral transformation processes in supercritical CO_2 provides a scientific basis involved in carbon capture and sequestration. ◆

The combustion of fossil fuels has led to a rapid increase of CO_2 emission, greatly contributing to global warming and causing adverse climatic and environmental changes. As global energy demand is projected to increase 57 percent by 2030, large-scale emissions will continue and even accelerate. Carbon capture and sequestration in oceans and deep geological formations such as underground saline formations, unused oil wells, and mining seams are promising to store freshly generated CO_2. Because of high temperature and pressure present in deep geological "vaults," the CO_2 is expected to exist as a supercritical fluid and remain as long as the cap rock remains intact. For the duration of the storage, the supercritical CO_2 will interact with saline solutions and electrolytes in the liquid phase and is expected to facilitate significant mineral transformation. The nature and amount of the resulting secondary minerals and the extent and rate of CO_2 conversion are influenced by several factors: pressure, temperature, surface hydration, liquid flow rate, mineral composition, pH, phase separation/formation, surface reaction, chemical composition, and interfacial diffusion.

Unfortunately, little is known about the physical and chemical processes that occur with supercritical CO_2 and water at solid-liquid and liquid-liquid interfaces. A thermodynamic database includes mostly aqueous phase phenomena with a limited amount of organic solvent data. Also, the scientific community lacks experimental infrastructure to address these complex issues at a process or molecular level. To address these deficiencies, we will develop an integrated supercritical fluid optical spectroscopy system, including ultraviolet visible absorption, laser induced time resolved fluorescence, and Fourier transform infrared spectroscopies as well as Raman, second harmonic, and sum frequency generations. The system will be capable of performing in situ optical spectroscopy measurements of mineral dehydration, dissolution, formation, sorption and desorption, and characterization of solid-liquid and liquid-liquid interfacial processes.

Based on an older supercritical fluid extraction system, a prototype supercritical fluid manipulation transmission mode infrared measurement system was set up. The system is capable of infrared measurements from ambient pressure to 4500 psi with temperature ranging up to 75°C in a 400 to 4000 cm^{-1} wavelength range. Concurrently, a second system is being designed and built that includes modular cell designs to allow optical spectroscopic measurements from reflection mode infrared, laser Raman, fluorescence spectroscopy, and the option of integration with optical microscopy and nonlinear optical spectroscopy. Control mechanisms are also developed so that the temperatures of liquid tubings and cell outside the oven housing the supercritical CO_2 system are regulated independently.

Using the developed supercritical CO_2 infrared spectroscopic system, we investigated H_2O/D_2O dissolution and speciation in supercritical CO_2. Results showed that H_2O and D_2O have unique infrared spectral features over a broad spectral range, and spectral intensity is proportional to the concentration of D_2O, allowing in situ D_2O quantification in supercritical CO_2. The dissolution kinetics depend on D_2O in supercritical CO_2, and there appears to be a slow drop in intensity at longer times accompanied with the appearance of a weak new spectral band at about 1400 cm^{-1}. Detailed analysis of the H_2O/D_2O spectra will help reveal mechanism of water interaction with supercritical CO_2.

Methods were designed and tested for making minerals (forsterite) thin films for infrared spectroscopic measurements in supercritical CO_2, including pressed powder flakes of ground Mg_2SiO_4 and opaque slurry film prepared using ground Mg_2SiO_4 and D_2O. The slurry was applied directly to ZnSe cell window and dried under N_2. Spectral analysis of the prepared thin films showed spectra similar to published spectra of Mg_2SiO_4, demonstrating the appropriateness of the techniques. Preliminary experiments with forsterite thin film interaction with supercritical CO_2 showed that the reaction occurred within a few hours, with possible conversion of forsterite into chemical species that bear signatures of Mg carbonates. However, spectral changes are complicated, and further experiments and detailed analyses are required to delineate the reaction processes.

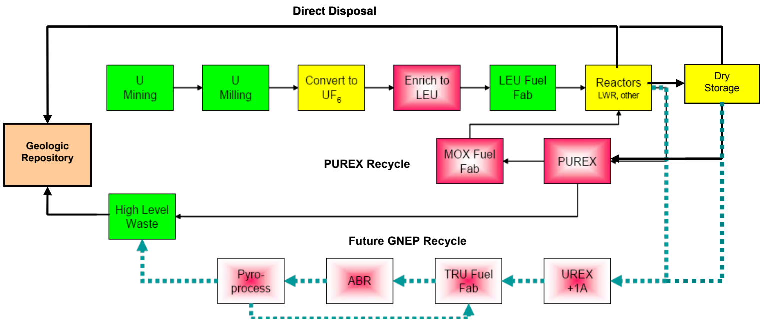
The above progresses set our research and development for FY 2010. We will continue in situ instrument development for integrated reflective mode Fourier transform infrared spectroscopy, Raman and fluorescence in supercritical CO_2, and complete solubility, speciation, and reactivity studies of water in supercritical CO_2 under different temperatures and pressures. We will commence spectroscopic investigation of forsterite and closely related minerals at variable temperature, pressure, H_2O/D_2O concentration, ionic strength and proton concentration.

Analytical Framework for Assessing the Economics of Reliable Fuel Services and Supply

Steven M. Short, Mark R. Weimar, Sean J. Kreyling, Zoe N. Gastelum, Julia B. Harvey

◆ We are developing an analytical construct and software toolkit to perform systematic comparative studies of reliable fuel services and supply options that will further the understanding of the economics and risks associated with potential reliable fuel services and supply offerings. ◆

Along with the anticipated global expansion of nuclear energy, concerns have been raised by the international nonproliferation community about the consequences of additional States acquiring enrichment and reprocessing technologies and know how as part of a nuclear energy program. These concerns are not new. Interest in creating policy measures to control the use of nuclear energy has been present since the 1940s and can be seen in the Atoms for Peace proposal initiated by President Eisenhower in 1953. Efforts to reach an international consensus on how to control and secure nuclear fuel supply were undertaken extensively during the 1970s and 1980s by the International Atomic Energy Agency to no avail. Desires to develop an international consensus have been rekindled by renewed international interest in nuclear power and recent international incidents involving States' development of enrichment and reprocessing capabilities outside of the nuclear nonproliferation treaty. At least 12 proposals (with additional expected) offering varying degrees of multinational or multilateral alternative reliable nuclear fuel services assurances have been made to date to the International Atomic Energy Agency by various nations and non governmental organizations.



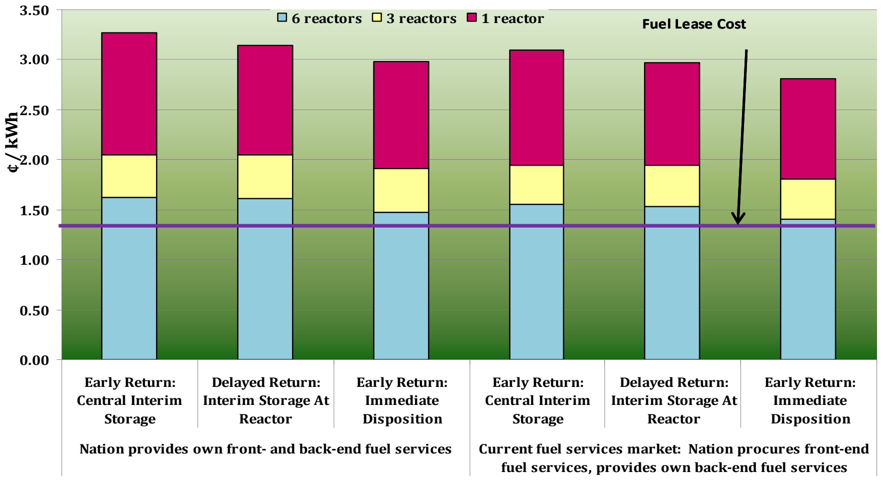
Nuclear fuel-cycle services.

PNNL is developing an analytical framework for consistently and systematically assessing the economics and nonproliferation merits of alternative reliable nuclear fuel services arrangements, including current and future proposals. This will entail development of a model having the flexibility to represent a variety of fuel types, nuclear fuel cycles, and nuclear power expansion projections. Because demonstrating the utility of the analytical framework and model is critical, a substantial portion of our efforts were directed toward assessing one specific reliable nuclear fuel services option: nuclear fuel leasing.

A cash flow model was developed having modules or components representing each major process in the nuclear fuel cycle using data and approaches predominantly already developed and available in the literature. The analytical framework provides the flexibility to assess the economic impact of alternative fuel supply (front end) regimes and alternative spent nuclear fuel disposition (back end) regimes. The analytical construct spans the entire breadth of the nuclear fuel cycle because the proposed reliable nuclear fuel services options range from providing reliable fuel supply on the front end to providing fuel cycle services on the back end, plus proposals for making fuel suppliers ultimately responsible for spent nuclear fuel management and disposition. The current version of the model only reflects modules for enrichment, dry storage of spent nuclear fuel, direct disposal, PUREX recycle facilities, and MOX fuel fabrication. Advanced fuel cycle modules are not currently incorporated, although the prototype model has been constructed with the flexibility to incorporate additional future modules.

The model's analytical framework identifies necessary fuel type, quantity, characteristics, and cost factors, and quantifies the cash flow analysis, economic analysis, and logic. The current analysis figures of merit include 1) total and incremental life cycle cost, cash flow (revenues and expenses), and unit cost based on constant dollar analysis and discounted dollars, 2) logistical attributes, such as total and annual metric tonnes heavy metal and facility requirements (number, capacity, timing, etc.), and 3) fuel characteristics (time since discharge, and burn-up). The model enables the user to manipulate many assumptions underlying the fuel cycle, including timing of each aspect of the fuel cycle, a limited number of reload durations (fuel enrichment and burn-up), current market prices, scaling factors for evaluating alternative sized facilities, number and size of power reactors, and rate of return for each privately owned facility in the fuel cycle. The end result is a model that allows the user to manipulate and determine the effects of many nuclear fuel cycle parameters on the economics of proposed reliable nuclear fuel services options. Currently, modules have only fuel leasing options, but the model does include all other fuel cycle services.

During FY 2009, three fuel services scenarios were evaluated to demonstrate the utility of the model and compare the cost of fuel leasing relative to the current nuclear fuel service market: 1) a nation obtains all front and back end fuel services (including spent nuclear fuel take back) through a full service fuel lease arrangement, 2) a nation provides its own front and back end fuel services, and 3) a nation procures its front end fuel services from a current fuel vendor and provides its own back end, which represents the current fuel service market. Each of the scenarios was evaluated for three different assumptions regarding back end fuel management approaches: 1) early return of spent nuclear fuel followed by interim storage for 50 years and subsequent disposition, 2) early return of spent nuclear fuel with immediate disposition, and 3) delayed return of spent nuclear fuel or 50 years of interim storage prior to return and disposition. The results are presented as a cost per unit of electricity produced for nations having one, three, and six power reactor programs.



Cost premium per kWh to acquire enrichment for potential lessee nations for closed fuel cycle options.

Another focus of the research conducted in FY 2009 was in developing an analytical framework and model for assessing the economics of reliable nuclear fuel services alternatives. The utility of the framework was demonstrated in an assessment of fuel leasing as a reliable nuclear fuel services alternative. The model results clearly show that for either open or closed fuel cycles, fuel leasing is preferred from an economic cost standpoint and that the cost premium or penalty for not using fuel leasing can be substantial. The analytical framework and analysis of fuel leasing were published for presentation at the Global 2009 conference.

While initial efforts were made to develop a metric for assessing the nonproliferation benefits of reliable nuclear fuel services arrangements, this will be a focus in FY 2010. Once developed, the nonproliferation metric will be integrated with the economic model. The goal in FY 2010 is to complete the prototype integrated model and demonstrate its utility as a tool for consistently and systematically assessing the economics and nonproliferation merits of alternative reliable nuclear fuel services arrangements.

Carbon Capture Process Modeling and Economic Evaluation Tool Development

Mark D. Bearden, Yunhua Zhu, Corinne Valkenburg, Sandra A. Tjokro-Rahardjo, Charles J. Freeman, Daryl R. Brown

◆ Useful carbon dioxide (CO_2) capture technology for coal fired power plants must integrate into the entire power generation system and provide economic advantage over alternatives. This project provides simulation tools to determine energy impacts of CO_2 capture. ◆

The objective of this project is to determine the value of improved CO_2 capture technology for fossil-fueled power plants. Other companies have generated technical and economic analysis based on coal and natural gas fired power plant simulations. Unfortunately, simulations that form the bases of these reports are proprietary and cannot be adapted by those engaged in developing improved CO_2 capture technology. This project was initiated to construct simulation tools that will provide: 1) material and energy balances, environmental performance, utility requirements, and some equipment sizing for entire power plants configured like the National Energy Technology Laboratory (NETL) benchmarks for integrated gasification combined cycle (IGCC, Selexol carbon capture) and supercritical pulverized coal (PC, Econamine [MEA] carbon capture), 2) modules simulating improved carbon capture technology under development that can be inserted into base power plant simulations, 3) current capture technology metrics that provide targets that new technology must exceed, 4) directions for experimentation, physical properties to obtain, and what components in the feed gas that must be dealt with, 5) an early-stage screening tool to identify technology that warrants further resource investment, and 6) operating cost estimates (including capital) for calibration with NETL benchmarks.

During FY 2009, modular power plant simulations using AspenPlus were developed for a supercritical pulverized coal plant using the MEA system for CO_2 capture. This simulation is divided into eight modules separated by function and physical property requirements. Each module containing the appropriate physical properties, chemical components, and operation models was developed separately and combined into a single simulation. Equipment, including heat exchangers, absorption towers, pumps, fans and compressors, are sized in the simulation to provide input for cost estimation.

All modules for an IGCC benchmark were developed, including slurry preparation, elevated pressure oxygen plant (to minimize compression requirements), gasification, shift reaction, Selexol with hydrogen sulfide concentration, gas turbine/heat recovery steam generator, steam cycle, Claus unit, CO_2 compression, cooling water system, and refrigeration (for Selexol). Tools to analyze solid sorbents for CO_2 capture and for economic analysis are being developed. Excel-based correlations for large power plant equipment such as field erected boilers and flue gas desulfurization units will be combined with Aspen data to generate total installed equipment cost estimates for the entire plant and supporting utilities.

There are numerous benefits to the structured approach to simulation development, including independent module construction by the development team, using specialized physical property models only where required and extending the flexibility of the model. For example, a supercritical steam cycle can be converted to a subcritical cycle by exchanging a single modules in the simulation, or the computationally intensive physical property calculations of electrolyte properties can be restricted to the MEA module where required. Using electrolyte physical properties, the MEA module of the base simulation may be removed and the CO_2 binding organic liquid (CO_2BOL) module inserted with appropriate adjustments to the chemical components and physical properties parameters.

Studies during FY 2009 included several specific capture technologies, such as CO_2BOLs, carbonate cycling, electrochemal switchable solvents, and cryogenic flue gas separation using specific modules, which were developed from the tool set. For CO_2BOLs, a module was built for incorporation into the IGCC plant model consisting of desulfurization with MDEA followed by adsorption drying, CO_2BOL formation in the absorber, and decomposition heating and pressure reduction. Compared to the Selexol benchmark, power consumption was lower but steam consumption higher. This model will be refined with the introduction of more experimental data in FY 2010.

In FY 2010, work will continue, including refinement of the models, specifically the assembly and operation of the IGCC benchmark, and development of economic analysis tools for benchmarks and other technology. We will also continue to refine the IGCC concept with MDEA and drying, develop a carbonate looping case, 1) perform an enzyme catalyzed analysis for liquid ammonia-water or amines after identifying the most promising candidate, 2) determine the appropriate case for simulation of electrochemical switchable solvents, 3) build power plant simulations with solid sorbents as data becomes available, and 4) perform incremental economic analysis of these technologies against NETL benchmarks. The exact work performed is conditional on which technologies can provide information suitable for determining operating performance and capital requirements for comparison to the benchmarks.

Carbonate Sorbents and Enzymatic Catalysts for Carbon Dioxide Capture

James R. Collett

◆ We are developing methods and materials for using the enzyme carbonic anhydrase to catalyze the capture of carbon dioxide (CO_2) from industrial post-combustion flue gases. This approach shows significant promise as a way to reduce greenhouse gas emissions from fossil fuel power plants in a cost-effective manner. ◆

We are developing carbonic anhydrase as a catalyst for use with ammonia-based chemical sorbents for post combustion CO_2 capture. Carbonic anhydrase catalyzes the hydration of CO_2 to yield bicarbonate by up to one million-fold. This novel approach has the potential to accelerate the kinetics of absorption and desorption of CO_2 by the ammonia sorbent, thereby reducing thermal energy requirements and the size and capital costs of unit operations at the plant scale. Ideally, the catalyst will be a "drop-in" additive for concentrated ammonia solvents that should require few modifications to the designs of existing absorber/regenerator hardware. Development of the catalyst will be performed on a laboratory-scale, bench-top absorber/regenerator system with the goal of continuously removing 90 percent of the CO_2 from simulated post combustion flue gas streams. From this work, we anticipate several additional outcomes: 1) a novel enzyme-ammonia absorber/stripper process for the capture of CO_2 from post-combustion flue gas streams, 2) methods and biochemical compositions of matter that maximize the performance of carbonic anhydrase enzyme catalysts in concentrated (between 2 and 6 M) aqueous ammonia solutions used for post combustion CO_2 capture, 3) formulations for aqueous ammonia solvents optimized for use with the enzyme catalyst and maximize the rate of CO_2 absorption and desorption from the solvent phase while minimizing thermal energy requirements, and 4) a rated-based Aspen process engineering model that demonstrates efficiency gains that may be possible by adding the enzyme catalyst to the circulating solvents used in current ammonia-based CO_2 capture absorber/stripper unit operations.

In FY 2008, we performed preliminary tests of the ability of carbonic anhydrase to catalyze the hydration of dissolved CO_2 in the presence of high concentrations of ammonia such as those used in the chilled ammonia and aqueous ammonia processes for CO_2 gas removal from flue gas streams. In these experiments, two continuously stirred tank reactors (CSTRs) containing 0.5 liter of 2.7 M NH_4OH + 0.9 M NH_4NO_3 maintained at 13°C were placed side-by-side and sparged with 15 percent CO_2 and 85 percent N_2 flowing at 0.5 liter per minute. One of the solutions (CA+) was amended with 77 mg of bovine carbonic anhydrase enzyme. The other solution (CA–) served as a control, and did not receive any enzyme. Below 9.0, the drop in pH was much faster in the CA+ solution than in the CA– solution, which indicated that the conversion of dissolved CO_2 to bicarbonate had been accelerated by carbonic anhydrase. The rapid pH drop also demonstrated that the activity of carbonic anhydrase enzyme may be maintained in highly concentrated ammonia solutions such as those used in the existing aqueous ammonia process.

In FY 2009, the experimental apparatus was improved with the addition of digital mass flow controllers and meters to control and account for mass balances. A LabVIEW data logging program was created to log pH, gas concentration, gas mass flow, gas pressure, gas temperature, and liquid sorbent temperature automatically during the experiments. Further studies in a Parr reactor CSTR and a 600-centimeter glass bubble contactor column were performed using 7 percent NH_4OH at 25°C to simulate more closely the absorption conditions of the aqueous ammonia process. Multiple tests showed that the enzyme provided an approximate 20 to 25 percent increase in the kinetics of hydration of CO_2 to yield bicarbonate as indicated by the time required for the pH to drop from 9.6 to 8.8 during sparging with 15 percent CO_2. Regeneration tests in a stainless steel trickle column indicated that effective thermal desorption of CO_2 from 7 percent ammonia does not begin until a temperature of about 65°C is attained, which is above the denaturing temperature of the bovine form of carbonic anhydrase that we used in our absorption tests. As such, we determined that a more thermostable form of carbonic anhydrase will be necessary if the enzyme is to be used as a dissolved "drop-in" catalyst for the aqueous ammonia process. To meet this requirement, the gene for the thermostable carbonic anhydrase from *Methanobacterium thermoautotrophicum* was introduced into *E. coli* for the recombinant production of this enzyme. Approximately 2130 mg of highly purified thermostable enzyme was produced and will be available for testing during FY 2010.

During FY 2010, enzyme kinetic data from the experiments above will be added to a rated-based Aspen Plus RateSep computer model to simulate absorber and regenerator column performance in the aqueous ammonia process. The model will be used to estimate potential efficiency gains in post-combustion CO_2 removal that might be realized at a 550-megawatt coal-fired power plant by adding dissolved carbonic anhydrase to an aqueous ammonia system.

Climate Feedbacks in the GCAM Integrated Assessment Modeling Framework

Allison M. Thomson, Benjamin Bond-Lamberty, Leon E. Clarke

◆ The impacts of a changing climate on human and natural systems are the basis for global climate change concerns. However, these impacts do not exist in isolation from society's efforts to reduce greenhouse gas emissions and adapt to a changing climate. Understanding the interactions between climate changes and human actions to address climate change is therefore necessary to make effective decisions regarding mitigation and adaptation. ◆

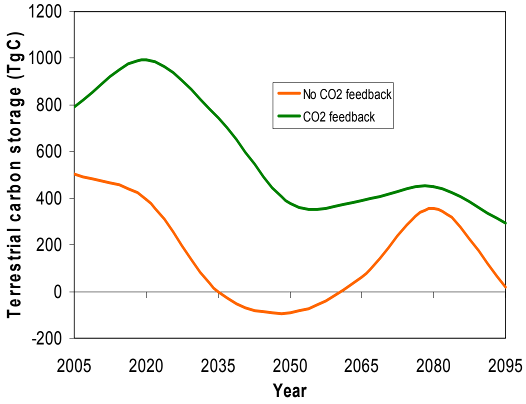
Simulation models that can integrate climate feedbacks, their impacts, and possible human actions to mitigate both the causes of climate change and the impacts are necessary tools for making effective mitigation and adaptation decisions. Integrated assessment models, including the PNNL Global Change Assessment Model (GCAM), are among the most important tools that decision makers rely on to inform climate mitigation decisions. Integrated assessment modeling is only beginning to address the feedbacks and their implications for impacts and adaptation.

The problem of climate feedbacks – the modification of climate by processes that themselves change with climate forcing – is critically important in climate studies and global system modeling. One well-known feedback involves the potential for CO_2 fertilization in which higher levels of atmospheric CO_2 permit more efficient photosynthesis by plants resulting in increasing carbon storage by ecosystems; this is negative feedback and has been intensively studied. To date, no integrated assessment model includes the effect of rising CO_2 on ecosystem carbon storage.

The objective of this project is to develop a version of GCAM that includes key climate feedbacks and to create a strong foundation for integration of GCAM with detailed process level models, global and regional climate and earth system models, and ecosystem models. The CO_2, temperature, and precipitation effects of the GCAM emissions scenarios for varying levels of climate mitigation will be looped back at each model time step and therefore act as drivers of each subsequent time steps ecosystem productivity, energy demands and supplies, water availability, and carbon cycling. This capability will enable analyses of the ecosystem and energy costs of climate change and associated and relative benefits of adaptation and mitigation policies and actions.

During FY 2009, feedback of global CO_2 concentration from the Model for the Assessment of Greenhouse-Gas Induced Climate Change (MAGICC) to the agriculture and land use module of GCAM was established. MAGICC is a separate model fully coupled to GCAM for simulation of the greenhouse gas concentrations and climate effects of the integrated assessment model emissions and land use scenarios. In addition, a methodology for incorporating this feedback dynamically, as model runs will be implemented and further expanded as capabilities include feedbacks from temperature and precipitation changes. This development will improve understanding how energy and land systems will evolve in a changing climate and position the GCAM to answer new questions and facilitate interaction with physical based global climate and earth system models.

The interface between GCAM and MAGICC was modified to allow for feedbacks at each model time step. After each 15 year time step is solved by the model, the MAGICC model is invoked to compute the net change in global CO_2 levels; this parameter is extracted from MAGICC and used to adjust ecosystem carbon contents by assuming a 20 percent rise in carbon storage under doubled CO_2 levels, consistent with many studies.



The coupled GCAM-MAGICC feedback of CO_2 results in higher levels of terrestrial carbon storage over time.

This feedback will become a component of the operational model. This modification results in dynamic response of the terrestrial carbon stocks and land use change emissions in GCAM to increasing atmospheric CO_2 over the century. Changes in CO_2 as projected by GCAM directly impact the changes in agricultural productivity simulated by GCAM. Similarly, carbon cycle components of GCAM are impacted by CO_2 induced changes in vegetation growth in forests and grasslands.

During FY 2010, we will build on this progress to include temperature feedbacks and resulting impacts on the land use and energy sectors of GCAM.

Electrolyte Development for Next Generation of Lithium Ion Batteries

Wu Xu, Ji-Guang (Jason) Zhang

◆ Plug-in hybrid and pure electric vehicles need energy storage systems to have higher energy density, longer cycle life and calendar life, higher safety, and lower cost than the state of the art lithium (Li) ion batteries. The development of new electrolytes will enable the use of high voltage cathodes and the success of silicon (Si) as anode materials for next generation of Li ion batteries to increase significantly the energy storage capacity of each single cell. ◆

Existing Li ion battery technologies have several drawbacks, such as limited energy storage capacity, high cost, limited cycle life, and some safety concerns especially at a voltage higher than 4.3 V versus Li^+/Li. To increase either the energy density of the batteries or the amount of charge stored reversibly per unit weight and volume of batteries, high voltage cathode materials and/or high capacity anode materials such as Si can be used. However, using of cathode materials with voltage above 4.5 V makes the electrolytes electrochemically unstable. On the other hand, using new anode materials with higher energy storage than carbonaceous materials faces a big volume change of the anode active particles during charge discharge cycles, causing disconnection of active particles and thus decreases capacity suddenly and sharply after several or dozens of cycles. Therefore, there is an urgent need to design and develop new electrolytes that allow the use of high voltage cathodes for the next generation Li ion batteries and enhance the stability of high energy anode materials.

In FY 2008, a through literature search was conducted and most key materials and chemicals were ordered. The preliminary electrochemical test on effect of salt additives on Si based electrodes reveal that the addition of 2 percent $NaPF_6$ in the control electrolyte leads to a lower capacity of Si based electrodes, while the addition of 2 percent KPF_6 improved capacity.

In FY 2009, by using semi empirical methods (Spartan 06 B3LYP/6-31 G* level software) to calculate the molecular orbital energies of commonly used carbonate solvents and their fluorinated counterparts, and performing experimental tests of cyclic voltammetry on electrolytes, we found that fluorination of a carbonate increases not only the oxidation but also reduction potential. However, the electrochemical stability window is not changed. Thus, even fluorinated carbonates can be used for high voltage cathode materials, as they are not stable for regular graphite and Si anode materials, meaning fluorinated carbonates can only be used in battery systems with anode materials whose reduction potential (such as $Li_4Ti_5O_{12}$) is much higher than graphite.

The charge/discharge cycling performance of a $Li/Li_3V_2(PO_4)_3$ half cell containing an electrolyte between 3.0 and 4.8 V shows an excellent reversible discharge capacity and capacity retention for at least 100 cycles, indicating that the electrolyte is quite stable up to 4.8 V. Thus, it is feasible to use the electrolytes in high voltage battery systems with a stable cathode material. This work was presented at the Large Lithium Ion Battery Technology and Application at Long Beach, CA, and one related paper was published in the Symposium and Poster Book.

Novel macroporous composite anode sheets have been developed by incorporating the high volume change anode particles into the conductive supporting materials to form porous structure. Cell performance tests of such porous composite anode sheets reveal improvement in the capacity and retention of materials. Additionally, the effect of different binders on the electrochemical and cell performance of graphite and Si anode materials were investigated by cyclic voltammetry and charge/discharge cycling tests. It is found that certain binder systems, such as sodium carboxymethyl cellulose have improved effects on the cell performance of both graphite and Si anodes over the poly(vinylidene fluoride) binder.

An amended task about electrolytes for Li/air batteries was added to the project this fiscal year. New electrolyte formulations were developed to improve the performance of Li/air batteries. An electrolyte additive such as 12-crown-4 at an addition of 15 percent by weight in the electrolyte was found to increase battery capacity significantly. Hybrid air electrodes were also developed to improve the discharge rate of Li/air batteries. The best result for the pouch type Li/air batteries is about 360 Wh/kg of total battery weight.

In FY 2010, new organic compounds and Li salts for high voltage cathode materials will be synthesized to improve the capacity, cycle life, and safety of Li ion batteries. The effect of particle size of Si powders, carbon coating, and binders as well as the effect of salts, solvents, and additives on the performance of Si based anodes will also be further investigated. The success of this project will enable a practical application of a novel cathode and anode and significantly improve the energy density and safety of Li ion batteries used for plug in hybrid and electric vehicle applications.

Enhance Control Technologies and HVAC System Capability in FEDS

James A. Dirks, Robert T. Dahowski, Andrew W. Piatt

◆ By 2030, one could reasonably assume that existing buildings will be consuming more than two-thirds of the nation's electricity. To address the issues of energy security, grid security/stability, and carbon emissions, existing building stock needs to be reviewed to determine a cost-effective reduction of energy consumption. ◆

Due to advances in building codes, technology development, and design practices it is reasonable to assume that the energy use intensity of these new buildings will be about half that of the average existing building. Furthermore, EIA projects that by 2030 buildings will be consuming 80 percent of the electricity in this country, and therefore it is reasonable to surmise that existing buildings (those in place now) will be consuming more than two-thirds of the nation's electricity. To address the issues of energy security, grid security/stability, and carbon emissions, existing building stock needs to be reviewed. This project is focused on developing further capabilities to a powerful energy management tool, the Facility Energy Decision System (FEDS) software, which focuses on modeling building system performance and determining the optimal retrofits for existing buildings.

This effort focused on the enhancement of an energy management tool, the FEDS software, which focuses on modeling building system performance and determining the optimal retrofits for existing buildings. This work expanded the capabilities of the FEDS software by increasing the breadth and depth of its HVAC modeling options. FEDS has been used to identify hundreds of millions of dollars of cost effective retrofit opportunities.

Despite the capabilities of this software, there remain limitations that impact our ability to model some relatively common building systems adequately and to consider some of the more energy and cost-effective retrofit options. Without overcoming these limitations, we are not able to identify the truly most life-cycle, cost-effective optimal retrofits for existing buildings. We added the following capabilities to the model: 1) economizers and heat recovery ventilators, 2) reheat systems, 3) variable air volume ventilation systems, and 4) demand controlled ventilation.

In order to account for the impact of the aforementioned systems, we needed to model the impacts of outdoor air humidity more accurately on peak demand days. A significant effort thus entailed completely revamping the weather data files and the modeling of humidity on extreme weather days. All of the FEDS weather station data files were generated for the United States, Canada, and sites in Japan and the Pacific.

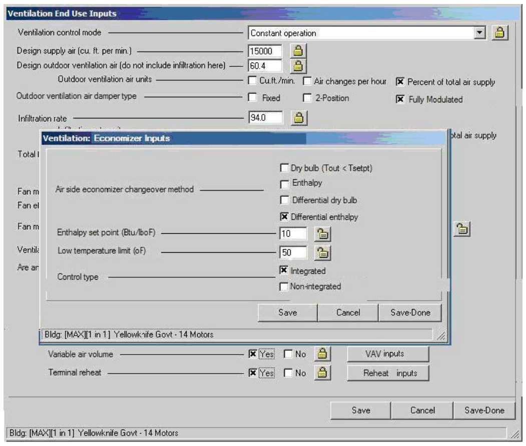
A number of key ventilation system options were added. Economizer modeling was completed with the following capabilities:

- four different changeover methods: dry bulb, enthalpy, differential dry bulb, differential enthalpy
- two damper types: continuously modulated or 2-position
- controls: integrated and non-integrated.

With these enhancements, the model can adjust the amount of outside air in response to the inside and outside conditions and the type of equipment present. This permits us to model the impact of economizers accurately.

Similarly, demand controlled ventilation (DCV) was modeled with the capability to adjust the outside air faction to values less than what is possible for building without DCV. When it is advantageous (e.g., outside air is extremely cold or extremely warm) and permissible (i.e., low occupancy) to decrease the outside air fraction, the model decreases the outside air fraction allowing us to model the impact of DCV accurately.

Central reheat (i.e., subcool reheat) was also added as a capability. This proved to be a very complex process to model as it requires simultaneous heating and cooling within a single time step. To model this technology accurately, it was necessary to determine the required absolute humidity in the conditioned space from the desired relative humidity and set point temperature. The supply air is then cooled to the dew point temperature in order to remove the humidity and then reheated to the desired temperature. Clearly, this was not only complex and difficult to model but in practice is also a relatively energy intensive process.


Ventilation End Use Inputs

Ventilation control mode: Constant operation
Design supply air (cu. ft. per min.): 15000
Design outdoor ventilation air (do not include infiltration here): 60.4
Outdoor ventilation air units: ☐ Cu.ft./min. ☐ Air changes per hour ☒ Percent of total air supply
Outdoor ventilation air damper type: ☐ Fixed ☐ 2-Position ☒ Fully Modulated
Infiltration rate: 94.0

Ventilation: Economizer Inputs

Air side economizer changeover method: ☐ Dry bulb (Tout < Tsetpt) ☐ Enthalpy ☐ Differential dry bulb ☒ Differential enthalpy
Enthalpy set point (Btu/lboF): 10
Low temperature limit (oF): 50
Control type: ☒ Integrated ☐ Non-integrated

Bldg: [MAX][1 in 1] Yellowknife Govt - 14 Motors

Variable air volume: ☒ Yes ☐ No
Terminal reheat: ☒ Yes ☐ No

Bldg: [MAX][1 in 1] Yellowknife Govt - 14 Motors

New ventilation system economizer inputs screen in FEDS.

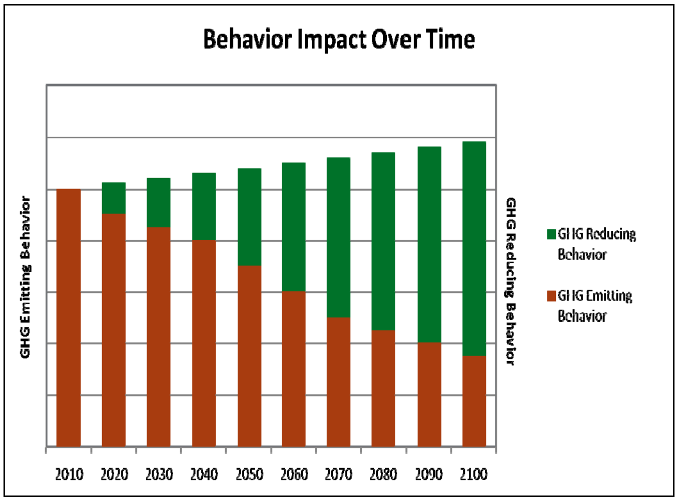
Impact of Energy Consumption and Technology on Global and National Energy Security

Lori L. Hobbs, Thomas F. Sanquist, Bin Shui, Heather M. Orr, Gariann M. Gelston

◆ This project intends to estimate U.S. consumer-based energy consumption to develop an understanding of potential future supply shortfalls (a grid vulnerability issue) and the impact of demand reduction interventions to reduce greenhouse gas (GHG) emissions. The specific benefits entail analyses of potential demand reduction interventions based on policies designed to influence consumer behavior without adversely affecting quality of life. ◆

Prior work in estimating the impact of consumer energy expenditure on GHG emissions has focused on relatively discrete forms of behavior (e.g., household electricity use) without considering the associated indirect costs of product manufacture, transport, and deployment. Our understanding of how to reduce consumption is restricted to point estimates based on small samples, and the impact over time is difficult to envision. While data do exist to suggest that consumer behavior is an important element of overall energy use and that it can be reduced, we do not have a clear understanding of how this might be manifested over time and in relation to national and international GHG reduction targets.

This project queries how much power consumption contributes to current GHG emissions and how much will it need to change and over what period of time to have a beneficial effect to avoid potential supply-demand mismatches. The ultimate goal is to assess behavior-based policies that will help the government and public to address dispassionately the means by which challenging GHG reduction targets will be achieved.



Form of behavior prediction model.

Our first year of research focused primarily on framing the problem in terms that are amenable to subsequent quantitative modeling. Integrated Assessment Climate modeling provides a basic framework for addressing behavior change in similar ways; that is, predicting changes in technologies and emissions over time. We intend to adapt knowledge of the technical potential for reducing energy consumption via behavior change (at the individual consumer or organizational level) to a forecasting model that will allow the assessment of changes in emissions over time. The primary project objective is to develop an engineering model of behavior and policy impacts on consumer-based energy consumption and GHG emission. The technical achievement will be a policy assessment tool that allows planners to understand potential targets for behavior-oriented policies and the likely effect of those policies over time. The targets will be identified through analysis of existing data compiled by DOE with an adaptation of Consumer Lifestyle Analysis and the effects of policy interventions assessed via time-based extrapolation of demand reduction effects demonstrated by previous studies.

Accomplishments during FY 2009 include the following: 1) compilation of relevant behavioral studies illustrating demand reductions achieved through means such as information, feedback, and regulation, 2) preliminary analysis of the 1997-2007 DOE Residential Energy Consumption Survey (RECS) data to illustrate growth patterns and potential target energy use behavior, and 3) evaluation of the potential GHG reductions resulting from expected increases in technical efficiency, such as net-zero housing, electric car penetration, and mass transit use. This latter activity suggests that the rate of technical efficiency change and penetration will not result in GHG reductions to the levels recommended by the Intergovernmental Panel on Climate Change, indicating that more aggressive approaches are required, including conservation and changes in the structure of consumer activity.

For FY 2010, we intend to develop the specific quantitative basis for various types of behavioral demand reduction interventions and address specific targets of energy use, such as air conditioning, commuter travel, and discretionary air travel. We will analyze RECS data at a regional level to identify variations in energy use across the country and underlying factors such as weather, population composition, and population growth. We will also evaluate a similar type of assessment for commercial buildings, as they constitute a considerable portion of energy use. The demand reduction interventions developed within the next year will be used as inputs to a grid vulnerability model that projects potential supply shortfalls.

Leveraging Scalable Demand Response Networks to Dramatically Enhance Carbon Emission Reductions

Robert G. Pratt, Thomas A. Ferryman, Jorge F. Reyes-Spindola

◆ This project seeks to develop a suite of technologies that will help utilities deliver massive amounts of energy efficiency cost-effectively as carbon management policies are adopted. The technologies use information from the interval metering, sensing, and control capabilities of the smart grid's demand response network to estimate carbon savings from efficiency measures adopted to each in a population of buildings. ◆

To gain credits for their efficiency efforts and prove program prudency to state regulators, utilities must measure and validate the savings efficacy of their efforts. The smart grid's demand response controls/sensors and communication network can be leveraged to measure end use efficiency savings and thereby help make efficiency programs more valuable to utilities. We propose to develop three applications to form the basis of a wide variety of tools and services that deliver added value to the consumer in the form of increased energy efficiency, energy cost reductions, and greater consumer control. We identified three critical capabilities that will be necessary: 1) American medical and demand response communication and controls to disaggregate load into major end uses, 2) building and updating models of customer loads for use in verification and diagnostics, and 3) measuring and verifying peak, energy, and cost savings by customer by end use.

A new capability in power grid monitoring has completed preliminary testing to be deployed throughout the United States. It is a modern demand response network with advanced metering infrastructure that will provide data at short intervals (hourly or less) and enable a much more temporal resolution with which to conduct accurate measurement and verification. The remote meter reading and communications capability of the network allow such readings to be collected and analyzed in near real time.

Three major goals for this project are to 1) develop disaggregation techniques based on short interval times series consumption data from advanced utility billing meters and control signals for major equipment engaged in demand response in commercial and residential buildings, 2) develop a technique for estimating savings from a statistical model of baseline consumption, and 3) for existing and new buildings, develop a technique for estimating savings based on extraction of equivalent thermal parameters. The project is intended to develop key components of a tool kit to enable the industry and consumers to control energy usage and achieve the benefits cited above.

Based on previously collected data, we investigated building analysis tools that would facilitate the industry to analyze demand response data and enable actions to reduce energy consumption, increase grid reliability, allow consumers to control costs, and reduce contributions to greenhouse gases. Little has been done in this area, as it is a new data source. To this end, data from the Early Lung Cancer Program pilot study (1986-1988) and Olympic Peninsula GridWise project was used and placed into analysis software. Data quality checks were made and disaggregation techniques investigated. Effort was placed on cleaning data, correcting errors, and organizing for analysis efforts.

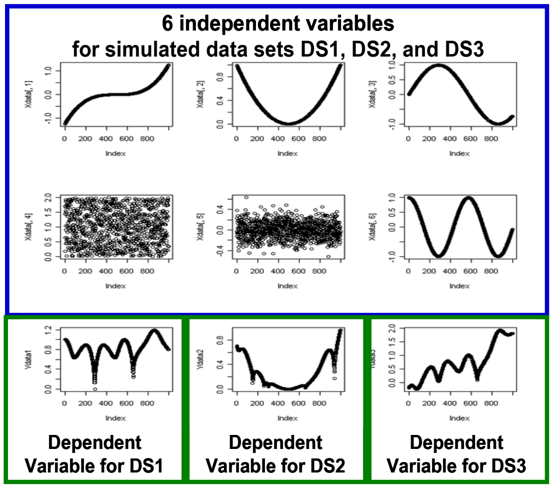


Illustration of three examples of the Y-Bin Method: six independent variables (top plots) are used to estimate three dependent variables (bottom plots). Accuracy of the estimates was good.

Work on the statistical model for data analysis focused on development of the Y-Bin Method, a novel process to enable estimation of dependent variables based on independent variables that may have significant nonlinearity and/or interactions. It provides a distinct capability not related to regression or other known techniques in use today or reported in the literature.

The outcome of this research will result in technology using the smart grid's measurement, control, and communications infrastructure. By leveraging communications and control capabilities of the grid, all carbon savings can be made measurable, verifiable, and fungible. Building these techniques into the grid's communication and billing network, the tabulation of carbon savings can be made routine and universal. This will result in the grid becoming the nexus for measurement and valuation of carbon savings from efficiency in buildings.

Marine Biomass and its Conversion to Liquid Transportation

Guritno Roesijadi, Michael H. Huesemann, Ronald M. Thom

◆ This research is intended to demonstrate the capability and provide findings to establish a path to a broader research and development program in marine biomass as feedstock for liquid transportation fuels. ◆

Seaweeds currently support a significant worldwide demand for food as well as polysaccharide based products for industry. Calculations show that recent annual commercial seaweed production of about 1.4 million dry metric tons is only 0.04 percent of potential annual production of the 3.5 billion dry metric tons available from just 1 percent of the ocean surface area. This potential compares favorably with the roughly 4.5 billion dry tons of plant biomass harvested from land. At present, consideration of macro algae as a biomass source for conversion to liquid biofuels is centered in Asia and Europe at an early stage of research and development. We propose studies intended to demonstrate capability and provide initial findings to establish a path for marine biomass to be used as feedstock for liquid transportation fuels. The long-term goal is a pilot- scale, offshore culture of macro algae and its conversion to liquid transportation fuels.

This project focuses on three interrelated aims: 1) through a review of known characteristics of macro algal species, identify candidate varieties with desired properties for both propagation and bioconversion, plus conduct field exercises for the collection of specimens, 2) initially using field collected specimens (and later specimens cultured in the laboratory), investigate the species' bioconversion into liquid transportation fuels, with a focus on determining the optimal microbial consortia for bioconversion and the seaweed species most suitable for bioconversion, and 3) conduct experiments on the propagation of seaweeds in the laboratory with the aim of improving propagation techniques for seaweeds suitable for bioconversion and testing the resilience of cultivated seaweeds to simulated oceanic conditions.

In FY 2009, we focused on demonstrating conversion to ethanol as an essential proof-of-concept for producing a liquid fuel using macro algae. Populations of the seaweed *Saccharina latissima* were sampled by SCUBA divers, and specimens were transferred to the laboratory for use in growth monitoring and as feedstock in ethanol conversion. Conditions at the laboratory were suitable for sustained seaweed growth. Individuals with an initial length of 19.9 cm exhibited a growth rate of roughly 1.4 cm/day, with an addition of 164 cm of new material over a 118 day observation period. Mannitol and laminarin (as part of total reducing sugars) are the main fermentable carbohydrates in *S. latissima* and were relatively stable in individuals maintained in the laboratory.

Preliminary experiments on conversion of mannitol to ethanol showed that the yeast *Pichia angophorae* converts mannitol to ethanol, a process that is enhanced by seaweed extracts. Ethanol production peaked between 3 and 5 days of incubation, possibly due to substrate depletion or further conversion of ethanol to acetic acid. In these fermentations, prior conditioning of *P. angophorae* with added mannitol in the inoculum is necessary for subsequent conversion of seaweed extracts to ethanol. While it is desirable to minimize the presence of oxygen to prevent the conversion of ethanol to acetic acid, *P. angophorae* cannot survive under strict anaerobic conditions. Thus, the improved culture conditions included prior conditioning of *P. angophorae* with mannitol and controlled aeration to meet the yeast's respiratory requirement, maintaining the need to limit the conversion of ethanol to acetic acid.

Fermentation of seaweed extract under optimized conditions demonstrated that the net ethanol yield from seaweed extract (as a function of mannitol consumption) is roughly equivalent to that of the mannitol supplemented incubations. Although more mannitol was consumed in supplemented fermentations, this led to a much greater production of acetic acid, indicating that a high mannitol substrate concentration facilitates the conversion of ethanol to acetic acid and decreases the net ethanol yield.

Subsequent years of this project will investigate the conversion to butanol, hydrothermal liquefaction to bio oils, and seaweed propagation and culture technologies for offshore cultivation.

	Mannitol		**Ethanol**	
	Mean Initial (g/L)	**Mean Final (g/L)**	**Production (mean max, g/L)**	**Yield (g/g)**
Mannitol medium	42.45±1.242	28.85±0.340	3.63±0.226	0.267±0.028
S. latissima extract	3.72±0.282	0.92±0.106	0.74±0.097	0.264±0.060
Extract + mannitol	45.46±2.635	22.50±0.960	7.80±0.566	0.340±0.046

Maximal ethanol yield of P. angophorae *cultures in mannitol medium* S. latissima *extract alone or extract plus mannitol during fermentation. Ethanol yields were calculated as a function of mannitol consumption (mean±1SE, n=3).*

Nano-Ribbon Membranes for Viable CO_2 Separation

Rick E. Williford, Hendrik Verweij (Ohio State University)

◆ Coal fired plants will continue to produce electricity for a long time, so there is a need for cheap and efficient CO_2 separation technology for this, and many similar, exhaust streams. This work considers a new type of membrane that targets the separation of CO_2 from flue gas mixtures in future coal plant designs. ◆

Coal plant flue gas contains 3-15 vol% CO_2 with the balance primarily N_2 and some H_2O. The DOE Carbon Sequestration Technology Roadmap goals are 90 percent CO_2 capture with less than 10 percent increase in energy cost by 2012. We consider flue gas as a mixture of CO_2 and N_2 and take effects of H2O into account. Membrane separation has a principal advantage that it can occur without external energy input, requiring no additional energy that would translate into operational costs. Because of harsh operating conditions, materials to accomplish the above goals must be developed. A key feature is the proposed ceramic membrane is stable and long lived in flue gas environments, thus minimizing downtime and replacement costs. Although porous ceramic membranes exist, they often require treatment with organics to achieve the proper surface chemistry to realize high separation. Treatment tends to plug the pores, which reduces permeance (throughput) and thus reduces efficiency important in industrial applications. The organic coatings are generally destroyed by harsh chemical and thermal conditions in exhaust gases.

The technical objective of this project was to produce a ceramic membrane that is stable in flue gas environments and provides a CO_2/N_2 separation factor greater than 10, along with high CO_2 permeance above 10^{-5} mole/m^2/Pa/sec, thus meeting DOE goals. The project scope encompassed a natural evolution from the laboratory bench to positioning for industrial applications in three years.

The membrane works because of two primary factors: small pore diameters and a specific pore wall chemistry. The small pore diameter restricts the permeation process to separate surface diffusion, thus excluding non-separative transport mechanisms. The pore surface chemistry assists by providing a higher affinity for CO_2 than N_2, thus loading pore surfaces with CO_2 and excluding N_2. High permanence is achieved by using a thin active membrane on porous support, with the latter for structural integrity. The membrane was developed using a technically diversified approach. One team pursued a nano-ribbon concept, where pores of the ceramic membrane were filled with a ceramic precursor, which then shrinks during calcination to leave 1 nm wide ribbon like pores along original pore walls. The second team was using another technique to coat the pore walls, thus reducing pore diameter to 1 nm. Both teams used the same materials to achieve similar surface chemistries.

Overall, the nano-ribbon team produced the better result. Throughout FYs 2008 and 2009, the teams' progress included developing the chemistries for applying the pore fillers, developing the dip coating and calcination processes to create the nano-ribbon pores, producing structurally robust membrane assemblies, obtaining preliminary results verifying separations over 30 percent higher than Knudsen transport mechanisms, and demonstrating high permeance of approximately 10^{-5} mole/m^2/Pa/sec.

In FY 2008, work indicated that a positive outcome could be expected for experimental verification. The low cost ceramic is suitable for high-temperature applications in flue gases and a variety of other exhaust streams. Membranes are expected to be stable for longer than 5000 hrs at flue gas temperatures for an estimated cost of less than \$500/m^2. A durable, cost-effective membrane for such applications greatly advances DOE's agenda for carbon sequestration. The most important result was demonstrating a combination of small pore diameter and specific pore wall chemistry, which provides the CO_2/N_2 separation and CO_2 permeance that will ultimately be needed for industrial applications.

During FY 2009, the focus was on eliminating the membrane defects that kept the separability under 10. A solution was found by applying a very thin coating of polydimethylsiloxane to the top surface of the membrane so that the pinhole defects were plugged without fatal reductions of the permeance. Polydimethylsiloxane can withstand temperatures of about 400°C, and thus should be robust in flue gas exhaust streams as long as the oxygen content is relatively low. A CO_2/N_2 separation factor α approaching 100 was demonstrated for a permeance of 3×10^{-9} mol/m^2/Pa/sec and α=5.3 for $7\text{x}10^{-7}$ mol/m^2/Pa/sec. Further refinements of polydimethylsiloxane thickness would likely produce the desired results of α=10 and 10^{-5} mol/m^2/Pa/sec.

The research team at PNNL is preparing several publications, including a journal article on molecular dynamics simulations indicating that separation factors between 10 and 35 are possible with CO_2 permeance over 10^{-4} mol/m^2/Pa/sec in support of the experimental work.

Novel Catalytic Route From Methanol/DME to Transportation Fuels

James F. White, Daniel R. Palo, Robert A. Dagle, Susanne B. Jones,
Jair A. Lizarazo-Adarme, Michel J. Gray

◆ The object of this research is to enhance the price of competitive syngas-based production of infrastructure ready transportation fuels from domestic feedstocks. This is to be done by simplifying the methanol to gasoline process, making it less capital-intensive and more economically viable in the production of gasoline and distillates from syngas via methanol. ◆

Methanol synthesis from syngas typically occurs at 50 to 70 atm and 260 to 320°C over a copper based catalyst. Methanol to gasoline synthesis typically operates 1 to 5 atm and 370 to 400°C over zeolite. Because the copper-based catalyst is unstable above 325°C and methanol to gasoline activity is too low at temperatures below 350°C, a methanol synthesis catalyst is needed that can stably operate at nearly the same temperature as the methanol to gasoline catalyst bed. This would enable a single reactor, one-step process to making gasoline from syngas, simplifying the process and improving heat management. Previous work on palladium-based catalysts resulted in the discovery of a highly active formulation for conversion of syngas to methanol. Unlike the conventional copper-based catalyst, it can operate in a temperature range compatible with methanol to gasoline synthesis. Further, this catalyst has been demonstrated to have thermal and catalytic stability at temperatures exceeding 400°C.

Pursuing a simplified process, we propose that this palladium-based catalyst could enable a one step syngas to gasoline process via the methanol to gasoline mechanism. This project will result in the development of tailored pentasil zeolite catalysts for the conversion of methanol/dimethyl ether to transportation fuel product with very low selectivity to durene (and other problematic side products). Modification of the zeolite catalyst will provide shape selectivity that drives production away from durene formation by means of size exclusion. An additional outcome of the project is an updated technoeconomic model of the process utilizing performance data from the new catalyst formulations. If found sufficiently favorable, the technoeconomic model results, will strengthen the technical argument based on catalyst formulation improvements.

Our project focused on three specific areas of investigation during FY 2009: 1) techno-economic analysis of the proposed one-step methanol to gasoline process, 2) demonstration of the methanol synthesis performance of the palladium-based catalyst compared with the copper catalyst, and 3) preliminary demonstration of the one-step synthesis using the palladium based catalyst coupled with zeolite methanol to gasoline catalyst in a single bed. The techno-economic analysis was conducted to assess the proposed process improvements on fuel synthesis economics. Three cases were modeled: 1) a base conventional fixed bed methanol to gasoline synthesis, 2) an improved catalyst one-step dimethyl ether synthesis followed by low pressure fluid bed methanol/dimethyl ether to gasoline production, and 3) a dual catalyst pressurized fixed bed system that combines methanol/dimethyl ether plus a zeolite catalyst for direct syngas conversion to gasoline. The results show that the gasoline production cost estimated for the third case can potentially reduce the base case cost by 25 to 30 percent. The second case potentially reduces costs by less than 10 percent due to difficult product separation.

Behavior of the palladium and commercial copper-based catalysts were compared directly by operating methanol synthesis from syngas in a fixed bed reactor at nominal pressure. The two catalysts were compared at similar temperature, pressure, and throughput. Because the copper-based catalyst is the industry standard for methanol synthesis plants, it serves as an excellent baseline for comparing the performance of the palladium based catalyst. At the lower temperature, palladium and copper had similar conversions, but copper had a higher methanol yield. At the higher temperature (more amenable to methanol to gasoline), the palladium catalyst had a higher conversion and nearly three times the methanol yield as the copper catalyst. As expected, the palladium catalyst showed improved performance at elevated temperatures compared with the copper catalyst.

Based on the high temperature behavior of the palladium-based catalyst, initial investigations of its use in conjunction with a zeolite methanol to gasoline catalyst were conducted. The mixture of the two catalysts, operating at temperatures from 300°C to 400°C, showed good carbon conversion, ranging from about 20 percent at low temperature to over 40 percent at higher temperatures, with less than a 10 percent methane selectivity at the highest conversions. Additional initial investigations probed the effect of bed configuration (i.e., the manner in which the catalysts are combined in the one step process). It was found that a combined bed performed much better than a sequential bed in terms of conversion and selectivity.

In FY 2010, activities will include updating the techno-economic analysis based on experimental results, modifying the palladium based catalyst to maximize methanol/dimethyl ether production, and improving the performance of the combined bed operation to produce gasoline from syngas.

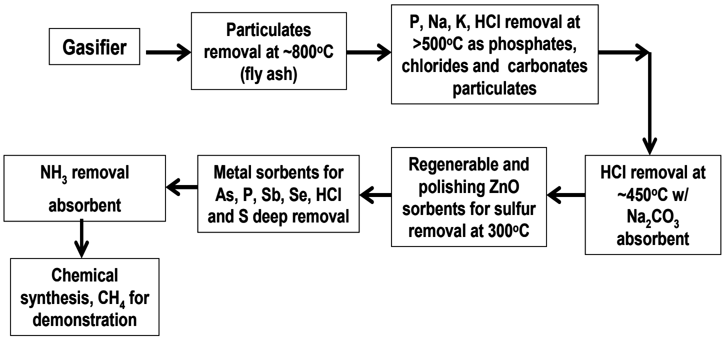
Overall Warm Coal Syngas Cleanup

Liyu Li, Baowei Chen, Christopher J. Howard, David L. King

◆ An integrated overall warm syngas cleanup system will be developed that can remove all the contaminants from warm coal syngas and thus protect downstream chemical synthesis catalysts. Compared with the conventional low temperature wet scrubbing followed by sacrificial guard bed system, this system will improve energy efficiency and simplify the operation process. ◆

Gasification of coal to syngas followed by catalytic synthesis of hydrocarbons or oxygenates provides a feasible strategy to meet the increasing demand for transportation fuels. This syngas has numerous impurities, including As, Be, Cd, Cl, Cr, Hg, K, N, Na, P, Pb, S, Sb, Se, V, and Zn. Most of these contaminants need to be removed down to part per billion levels due to their strong interactions with synthesis catalysts. Although technical approaches exist for removal of these species, they are rather costly, employing solvents at ambient or lower temperature and backup sacrificial sorbents. The energy efficiency of the current process would be improved if all the contaminants could be removed at temperatures higher than those of the chemical synthesis reaction (greater than 200°C).

The objective of this project is to develop an overall warm coal syngas cleanup system consisting of: a particulate filter to remove condensed species, a high capacity sacrificial absorption bed to remove HCl, two sequential ZnO beds to remove sulfur, a high capacity sacrificial absorbent to remove other volatiles, and a high capacity regenerable absorbent to remove NH_3 down to less than 10 ppm. Each subsystem will be individually developed and will be integrated together to demonstrate overall efficiency, although they can also be used separately for interested contaminants removal. This integrated system will be able to remove all the catalysts poisons in warm coal syngas and thus prevent the downstream synthesis catalysts from being deactivated.



High level flow sheet of total contaminants cleanup from warm coal syngas.

Progress during FY 2009 is described below.

At high temperatures (600-700°C), PH_3 is not stable and is oxidized to phosphorus oxides. These oxides react with alkaline metal salts (carbonates or chlorides) in the syngas and form alkaline metal phosphates, which can be removed by a particulate filter downstream at about 600°C. This chemistry of PH_3 also suggests that alkaline metal salts are good bulk PH_3 absorbents. A commercial Na_2CO_3 material was found to be able to remove HCl effectively. At 450°C, this Na_2CO_3 absorbent removes HCl in syngas from 100 ppm down to less than 1 ppm, with 50 wt% capacity. Surprisingly, K_2CO_3 was found to have very poor HCl removal performance under same conditions.

Fresh commercial ZnO absorbents were found to be able to remove sulfur (both H_2S and COS) from syngas down to less than 50 ppb with 15 wt% capacity. However, after regeneration, the same ZnO absorbent only removes H_2S and/or COS down to the several ppm levels, which is too high for the downstream synthesis catalysts or fuel cell applications. These understandings support our two sequential ZnO beds concept for sulfur removal: the upstream one as a regenerable bed for bulk sulfur removal and the downstream one as a sulfur polisher.

By trapping metal (nickel-copper alloy) nanoparticles in cubic mesostructured silica SBA-16 previously, we have developed a class of regenerable adsorbents that efficiently capture low ppm level of sulfur from warm syngases. During FY 2009, we found that this material could also effectively remove AsH_3 and PH_3 from warm syngas down to less than 1 ppb level, with 30 wt% capacity for AsH_3 and 6.5 wt% capacity for PH_3.

Planned future work for FY 2010 on this project will be focused on developing a high capacity regenerable absorbent that can remove NH_3 in warm syngas down to less than 10 ppm level, building up an integrated overall cleanup system, and testing the effectiveness of such a system using real warm syngas from a coal gasifier and using methanation as a model reaction. Our test results will be fed into a process simulation model to quantify the potential advantages of warm coal gas overall cleanup process over the commercial low temperature Rectisol process.

Predicting the Impact of Climate Change on U.S. Power Grids and its Wider Implications on National Security

Pak Chung Wong, Lai-Yung (Ruby) Leung, Ning Lu, Michael J. Scott, James Correia, Weilin Jiang, Chunlian Jin, Patrick S. Mackey, Mia L. Paget, Z. Todd Taylor, Yulong Xie, Jianhua Xu

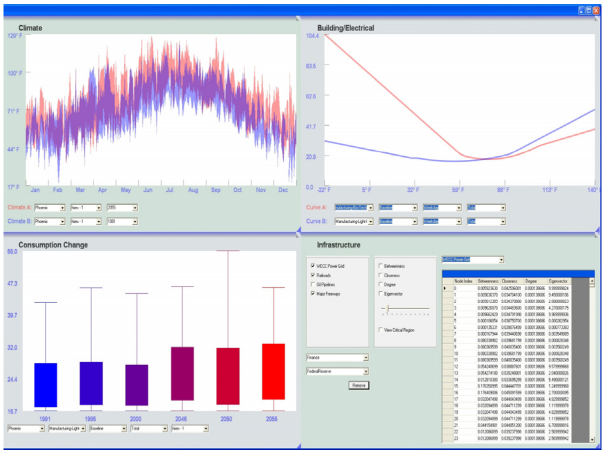
◆ This research extends modeling theories from climate, energy, social, and security domains to predict viable future technosocial scenarios for policymakers to formulate a unified strategy for building a secure society. ◆

We model and predict the impact of climate change on U.S. power grid and the wider implications on society and national security. For example, increased atmospheric temperature increases electricity consumption and affects precipitation, which changes the natural hydrological process and thus hydroelectric generation. It also affects wind electricity generation. Together, these energy demands could adversely affect the U.S. power grid and cause a widespread outage. If the outage persisted, it would impair the performance of our entire critical infrastructure and could cripple society. In this project, we investigated the potential impact of these changes from both technical and social perspectives. These project's activities were conducted sequentially. Lead components were completed to a degree that provided sufficient groundwork for the next component to be initiated before returning to refine the component models.

In FY 2008, we finished the climate analytical work on temperature modeling and completed most of the building energy simulations required for the power grid simulation. We also focused on the impacts of demographic and technological changes. We developed a visual analytics system prototype GreenOracle to guide analysis among domain components and present results. We finished the first simulation of climate change's impact on the power grid based on a typical meteorological year. The results suggested a potential western power grid vulnerability in the southwestern United States in the next 50 years.

During FY 2009, we developed a modeling approach to quantify climate change impacts on energy consumption, peak load, and load composition of residential and commercial buildings. This research focuses on addressing the impact of temperature changes on building cooling load in 10 United States and Canadian cities. Our results show that by mid-century, building yearly energy consumption and peak load will increase in the southwest. Moreover, peak load months will extend beyond summer into spring and autumn, with the Pacific Northwest experiencing more hot days in summer. Penetration levels of air conditioning systems in this region will likely increase significantly; as a result, some locations in the Pacific Northwest may shift from winter to summer peaking. The western states grid may see more simultaneous peaks across the north and south during summer months. Increased cooling load will result in a significant increase in motor load, which consumes more reactive power and requires stronger voltage support from the grid. This study suggests an increasing need for the industry to implement new technology to improve temperature sensitive load efficiency and apply proper protection to prevent adverse impacts of air conditioner motor loads.

We expanded GreenOracle so that scientists could collaboratively analyze their data and present results through visualization. For example, we linked power grid modeling results with critical infrastructure networks to identify the top cities/regions that would be most affected by climate change in mid century. We published six peer reviewed publications: two IEEE journal papers, one AAAI conference papers, and three other international conference papers) in 2009 detailing results from FYs 2008 and 2009.



Climate A: Phoenix, hires - 1, 2055
Climate B: Phoenix, hires - 1, 1991

Curve A: nufacturing-Bio-Tech, Baseline, Weekday, Total
Curve B: Manufacturing-Light-I, Baseline, Weekday, Total

Phoenix, Manufacturing-Light-, Baseline, Total, hires - 1

☑ WECC Power Grid
☑ Railroads
☐ Oil Pipelines
☑ Major Freeways

☐ Betweenness
☐ Closeness
☐ Degree
☐ Eigenvector
☐ View Critical Region

Finance
FederalReserve
WECC Power Grid

GreenOracle screenshots showing a simulation example.

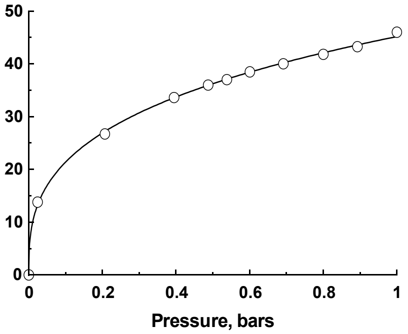
We will continue our work with a new social behavioral model and demand reduction interventions approach in FY 2010. The project will address technological and social aspects of climate change induced issues, including increased power demand and the need to reduce emissions to comply with policy targets. Population growth, regional climate effects, power demand, and emissions reduction are sufficiently complex that modeling interrelationships is needed to determine appropriate policy and technical approaches to potential future scenarios. It is inadequate to assume that power demand will be met; it is more likely that demand needs to be moderated by various interventions and met with a range of cleaner generating alternatives.

Prussian Blue Analogues and Interpenetrated Metal-Organic Frameworks for CO_2 Capture

Praveen K. Thallapally, Radha Kishan Motkuri, B. Peter McGrail

◆ We will design and develop low cost solid sorbents based on metal organic porphyrin (MOP) and zeolite imidazole frameworks (ZIFs) that capture CO_2 selectively over nitrogen and water at room temperature and 1 bar pressure. ◆

When producing electricity from coal, the promise of low CO_2 emission can be accomplished only if the CO_2 is economically captured. This approach would require the isolation of a relatively pure stream of CO_2 from coal combustion or gasification plants. Small-scale commercial systems use an amine based scrubber; however, significant cost factors associated with the amine processes are degradation of the solvent from reaction with O_2 (and other gases) in the flue gas stream and the energy input required for solvent regeneration. In addition, monoethanolamine-based amines, such as used in the Econamine FG process by Fluor have CO_2 loadings at 7 wt%. The inherent limitation in CO_2 loading in these solvents is an important limiting factor affecting CO_2 capture economics. Therefore, we focused on a new class of porous metal organic or ZIFs for CO_2 capture applications. Due to the high surface area, thermal stability and fine tuning the pore size make these materials attractive for CO_2 separation applications.



Uptake of CO_2 saturated with water at room temperature and 1 bar of CO_2. The CO_2 uptake shows approximately 9 wt%.

In the present work, we chose porphyrin and imidazole ligands 5,10,15,20-tetracarboxy porphyrin as molecular building blocks for construction of MOPs and ZIFs. We successfully synthesized MOP-2 with zinc, bypyridine, and ligand porphyrin by employing hydro(solvent)thermal conditions. Grown in a static autoclave at 200°C under autogenous pressure for 48 h, the crystals of all these products are stable in air for several days and insoluble in water. The powder x-ray diffraction of MOP-2 after solvent removal indicated no major change. Thermogravimetric analysis revealed that guest molecules were liberated below 200°C, though the crystal lattice is thermally stable up to 400°C. The MOPs showed 30 percent weight loss between room temperature and 250°C that corresponds with solvent molecule loss.

In order to obtain the absorption and desorption kinetics of various gases, MOPs were activated separately under vacuum at high temperature and placed in an HPVA-100 volumetric analyzer for gas sorption experiments at room temperature. Around 110 mg was placed in a sample chamber, and volume adsorbed per gram was plotted against CO_2 pressure. At low pressure, the calculated CO_2 weight percentage was 10 percent for MOP-2, which is comparable to existing metal organic frameworks. It is important to note that despite the microporous nature of the material, the metal centers in ligand play a major role in the sorption process. However, the majority of the metal organic frameworks and related systems focused on achieving high mass loadings, and very few publications dealt with selectivity. In this regard, MOPs were explored further to identify the selectivity toward nitrogen, methane, and hydrogen. Experiments with all pure gases at low pressures (1 bar) were shown to sorb very little or no uptake of nitrogen, hydrogen, and methane.

The effects of trace contamination on host framework were also studied. At close to 1 bar of equilibrium pressure, MOP sorbs about 22 percent of SO_2 and 8 percent of H_2S under similar pressure. The uptake of SO_2 is significant, as it sorbs 7 wt% at 0.1 bar pressure. Similar experiments with CO_2 saturated water were performed using the same sample at room temperature and 1 bar pressure. MOP sorbed 9 wt% of CO_2 with saturated water; however, analysis of the same sample after CO_2 saturated experiments suggested a loss of water molecule from the host cavity between 40 and 60°C. These results indicated that MOP has the ability to uptake CO_2 in presence of water without affecting capacity explained by the presence of hydrophilic and hydrophobic pockets inside the framework. The absorption heats for MOP calculated using a high pressure calorimetric apparatus were 75 Btu/lb of CO_2, which is 4 to 5 times smaller than monoethanolamine at identical conditions.

These results suggest that MOPs have the ability to capture and separate CO_2 more efficiently than related materials. Future studies will include material scale-up, demonstrating properties in bench scale and fine tuning material porosity to uptake more CO_2 at 0.15 bar pressure. We will also study sorption experiments by feeding a mixture of gases at once with a new multi component gravimetric gas analyzer coupled with mass spectrometry.

Self-Correcting Controls for Heating, Ventilation, and Air Conditioning Systems

Srinivas Katipamula, Michael R. Brambley

◆ Automated commissioning and self-correcting controls could substantially reduce the associated cost and help secure persistence of efficient operations leading to significant energy and cost savings to American taxpayers. This project developed a laboratory critical to achieving groundbreaking developments, leading to self-correcting controls and automated commissioning. ◆

Commercial buildings in the United States are often poorly operated and maintained, resulting in avoidable increases in energy consumption. While periodic automated commissioning can help alleviate the deficiencies with traditional operations and maintenance, the cost of manual commissioning has limited the automated version in the commercial buildings sector. Several studies have shown that poor operations and maintenance practices in commercial buildings lead to energy waste and emissions penalties between 10 and 30 percent. If these operating problems were eliminated, the benefits could yield reductions of up to 4 quads of energy and up to 240 million metric tons of carbon dioxide per year in the United States alone.

A number of organizations, including DOE and the California Energy Commission, are focusing research and development toward net-zero energy homes and commercial buildings. Although net-zero homes are technically feasible with today’s technology in some climate locations, significant improvements in efficiency are needed for broader adoption in the renewable generation technologies and the buildings and their systems. Current practice is to put photovoltaic cells on rooftops to generate power and in turn create power from geothermal sources. For significant penetration of net-zero energy homes and commercial buildings, the cost of the renewable generation technology must be lowered. Seeking net-zero energy at the community scale opens the possibility of using other renewable generation technologies, such as solar thermal electricity generation, solar-assisted heating/cooling systems, battery storage on site, hydrolysis, and wind energy. Further, community scale energy storage might be used cost effectively by decreasing the demand for peak electric power. These technologies cannot be easily deployed in a single home or a commercial building. If focus shifts a single net-zero energy home or commercial building, alternate renewable power sources are technically feasible and potentially practical at a community level.

The push for net-zero energy homes and buildings has significant repercussions to the stability and reliability of the electric grid. It is anticipated that the onsite generation technology will introduce additional volatility to the load profile. The expected increase in the volatility of a future net-zero load challenges the transmission and distribution system planning process. Operators already expect difficulty to integrate intermittent wind energy into the grid because of the unpredictable nature of the resource and the fact that generation is completely decoupled from load. The introduction of large numbers of net-zero energy homes and buildings are likely to exacerbate the problem of renewable integration if there is not early, careful planning and recognition of the interactions.

For our project in FY 2008, laboratory space was acquired and an air-handling unit, along with the necessary instrumentation and controls, was installed. Progress was made to demonstrate the real world feasibility of self-correcting controls; therefore, a testbed was created to develop, test, and demonstrate the controls in a laboratory environment. Additionally, a software framework to deploy and test self-correcting control algorithms was developed using temperature sensor problems as a basis.

A number of faults (temperature and humidity sensors, damper, and valve) have been selected for instigation. Significant progress has been made in positioning PNNL as a pioneering lab in development of self-correcting controls. Setup of the controls laboratory and development of the software framework to test self-correcting controls has positioned PNNL to attract programmatic funding from DOE and from other agencies such as the Bonneville Power Administration and the California Institute of Energy Efficiency.

During FY 2009, an air cooled chiller was integrated with the air handling unit, complete with upgraded controls. Three variable air volume terminal units have also been added to the air handling unit. In addition, standard control sequences have been implemented to control each of the implemented equipment components: the air-handling unit, variable air volume boxes, and the chiller. A network based user interface has been developed to enable implementation and management of experiments and streamlined recording and playback of data time series.

This research has resulted in enhanced PNNL capabilities in developing self-correcting controls for heating, ventilation, and air conditioning systems. Accomplishments throughout this fiscal year have included the completion of the laboratory testbed to develop, test, and demonstrate the self-correcting controls. We also developed an additional self-correcting control algorithms for an air handling unit and control problems (e.g., for dampers and valves).

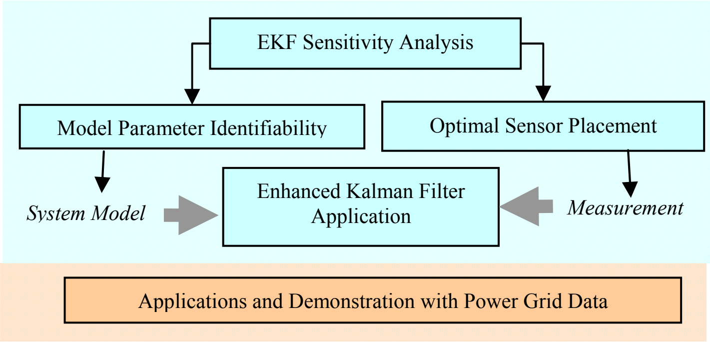
Sensitivity Analysis of Kalman Filter Applications in Power Systems

Zhenyu Huang

◆ This project aims to investigate the sensitivity properties of the Kalman filter to determine power grid observability and model parameter identifiability used to determine optimal sensor placement and model parameter calibration, respectively. The success of the proposed work will significantly improve the performance of dynamic state estimation and other power grid applications. ◆

Power systems pose fundamental challenges in real-time operations and control because they are highly dynamic with a large number of interacting, severe nonlinearity elements. Today's tools for real-time grid operations are mostly based on steady state models with response time in minutes, unable to capture the dynamic nature and too slow to prevent system failures. Tackling this challenge, the extended Kalman filter (EKF) can estimate power grid dynamic states based on a dynamic model and high-speed sensor data. Two of the key success factors in dynamic state estimation are the dynamic model quality and sensor locations. Given the complexity of power grids, the large number of candidate sensor locations and model parameters are not of the same importance in terms of the quality of the estimated dynamic states. Identifying key locations and parameters is an immediate need in the power grid dynamic state estimation application.

As a new scope different from application-oriented dynamic state estimation development, this work will focus on fundamental underlining mathematics of the Kalman filter and derive sensitivity information from its formulation, which will be applied to identify key locations for sensor placement and key model parameters for calibration. The resulting capability of optimal sensor placement and model parameter calibration will lead to significant performance improvement of dynamic state estimation for real-time power grid operation. The derived sensitivity property of Kalman filter is applicable to other engineering domains.



In FY 2009, efforts were focused on exploratory studies of the sensitivity formulation of EKF and numeric experiments on sensitivity using power grid models and data. We explored two approaches for formulating Kalman filter sensitivity and performed numeric studies of sensitivities associated with power plant parameter calibration. Our first approach, trajectory sensitivity analysis, quantifies sensitivities of a variable with respect to a parameter for a time-series trajectory (instead of a steady-state condition) of that variable. For each data point on the trajectory, a small perturbation of parameters is performed. Assuming a linear vicinity of the data point, the variation of the variable can be calculated, and the sensitivity of the variable with respect to the parameter is defined as the ratio of the variation and the perturbation of the parameter. In this way, the approach can capture the time variant nature of the sensitivity, and a performance index can be defined to measure the impact of the parameter on the variable, which in turn quantifies the parameter importance. Trajectory sensitivity analysis is a direct method but requires heavy computation to perform parameter perturbation.

The second Kalman gain-based approach uses the information contained in the Kalman gain matrix, which has already been computed in a regular Kalman filtering process. Mathematical derivation reveals that sensitivity with respect to a certain parameter is actually an element in the Kalman gain matrix. Each column of the Kalman gain indicates the importance of the corresponding measurement quantity, and each row indicates the observability of the state variable which is to be estimated or calibrated. A performance index similar to the trajectory sensitivity analysis can be defined to quantify the sensitivity level. This approach also considers the trajectory but can significantly reduce computation burden compared to the trajectory sensitivity analysis approach.

In calibrating power plant model parameters using EKF, we have been working toward researching identifiable model parameters. Numerical experiments have been performed using a generator model extracted from the western U.S. power grid. The results show that trajectory based sensitivities associated with generator model parameters are different based on the approach. Some with high sensitivities are identifiable parameters with select measurements, and some with low sensitivity are not identifiable. It is helpful to analyze observability of different parameters and identify those most influential to system dynamics. Our research effort will continue to exploit more options to measure the sensitivity of model parameters.

In FY 2010, the effort will continue the sensitivity formulation and analysis toward the application of Kalman filter to power system dynamic state estimation. This novel technique will be the first of this kind to track dynamically the status of the power grid in real time.

Tools for Evaluation of Net-Zero Community Concept and Integration of Buildings, Renewables and the Grid

Srinivas Katipamula, James A. Dirks, Michael R. Brambley, Nick Fernandez

◆ Numerous organizations are focused on promoting net-zero homes and buildings. Although technically feasible with today's technology in some climate locations, significant efficiency improvements are needed for broader adoption with renewable generation technologies and the buildings and their systems. Seeking net-zero energy at the community scale creates possibility of using other renewable generation technologies, such as solar thermal electricity generation, solar-assisted heating/cooling systems, hydrolysis, and wind energy. ◆

Buildings use over 40 percent total energy and over 70 percent electricity in the United States. Any solutions developed to reduce fossil fuels and carbon emissions will need significant contributions from the buildings sector. Through its Building Technologies Program, DOE has established an aggressive strategic goal to create technologies and design approaches that enable net-zero energy buildings at low incremental cost by 2025. High penetration of net-zero energy buildings/communities with significant distributed renewable power can have adverse effect on the stability and reliability of the grid.

A simplified analysis to highlight the advantages of net-zero energy communities as opposed to communities with individual net-zero energy buildings was conducted as part of our study. In addition, the project identified simulation tools that can be used to conduct a more detailed and thorough analysis of the two concepts. The project also developed a simulation framework for conducting detailed energy and power demand estimations for net-zero energy buildings and high-performance buildings. This framework would allow users to assess the impact of the high penetration of net-zero buildings and high performance buildings to the electric grid.

Expected outcomes for this project are as follows:

- Identification of simulation tools to conduct detailed analyses of a community net-zero energy concept.
- Development of a simulation framework for conducting detailed energy, power demand, analyses for community scale net-zero energy concepts and accessing net-zero energy building (including distributed renewable power generation) and energy efficiency impacts on the grid.
- Implementation of a framework that allows users to simulate a large number of buildings within EnergyPlus that represent either a net-zero energy community or a large number of independent net-zero energy buildings (residential and commercial).
- Presentation of a white paper encouraging net-zero energy communities and a comparison of the community net-zero energy concept with a concept with reliance on individual net-zero energy buildings.
- Enhancing our capability in analyzing net-zero energy concepts and positioning for future business.

Our major accomplishment in FY 2009 was developing a meta-tool for modeling high-performance buildings and net-zero energy buildings. This tool combines the functionalities of a number of existing tools, allowing a user to produce a series of building models using a limited number of inputs, from which hourly energy profiles are collected into a single file and used for further analysis. In addition, we formulated a simplified economic analysis that compared the levelized cost of generating power in a net-zero energy community and a community with individual net-zero buildings. Five scenarios were evaluated, including the base case (a community of net-zero energy buildings severed by roof-mounted photovoltaic cells) and four community scale net-zero energy building options served by wind turbines on leased land, wind turbines on owned land, a solar thermal electric generation, and a photovoltaic farm. Options assumed high-performance buildings for all scenarios (i.e., 70 percent more efficient than current construction practice).

Each of the above scenarios was compared with the base cases in two different diverse climate locations (Chicago and Phoenix). The levelized cost of electricity for each scenario was estimated and compared. The results from this analysis showed that even for the best case in the United States (Phoenix) for net-zero energy buildings, there are cost effective approaches to achieving net-zero energy than the conventional suite of technologies (rooftop photovoltaic with aggressive efficiency measures) used at the building level. By expanding the conceptual boundary for the net-zero configuration, a community can take advantage of scale economies and have other generation options at its disposal.

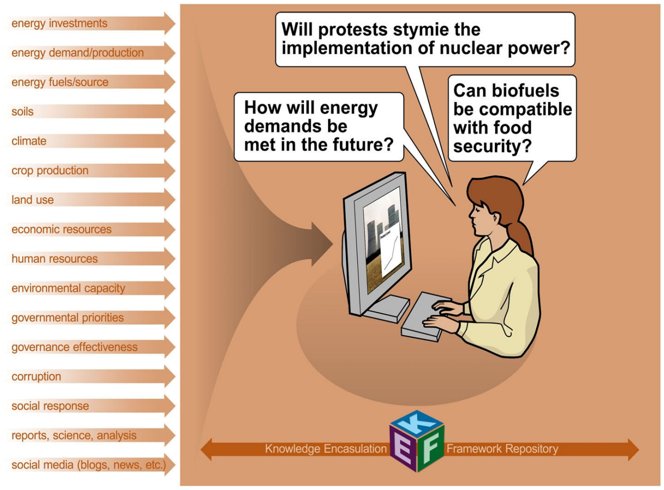
The proposed work for FY 2010 includes completion of the development and implementation of the simulation framework, extending the analysis of comparisons of the two net-zero energy concepts with additional scenarios (more detailed), and analysis of the impact of high penetration of net-zero energy buildings/community on the electric distribution and transmission grid using PROMOD.

Vulnerability of Food Security and Energy Infrastructure to Climate Change and Terrorism

Elizabeth L. Malone, R. Cesar Izaurralde, Larry G. Morgan, Antoinette L. Brenkert, Alison Delgado

◆ Questions about the effects of climate change policies in spheres important to national security can be comprehensively addressed using an integrative, technosocial model that connects knowledge about food security, energy production, and national security. ◆

A need for integration of knowledge domains has long been recognized. This project draws on three existing PNNL developed models: 1) MiniCAM, an integrated assessment model designed to examine greenhouse gas emissions, climate change, and mitigation scenarios, 2) EPIC, a watershed scale biophysical model used to examine agriculture (management as well as yield and productivity) and ecosystems, and 3) VRIM, an indicators model that produces comparative assessments of social and environmental resilience to climate change. Governance factors are also being modeled, and political and intelligence analysts have identified government will and effectiveness as important for assessing a country's capacity to address food security, energy issues, national security, and climate change.



A user of the model gains the benefits of multiple knowledge streams (left) gathered and organized in the KEF and integrated to address specific questions, such as how much a biofuels program might be expanded without causing food shortages and associated unrest, or whether nuclear power can be successfully implemented in an energy technology portfolio.

This project advances research into integration of disparate knowledge, pushing the frontier of science with decision support relevance. While accounting for impacts in multiple areas, the ability to explore alternative futures to date has been undertaken principally in qualitative analyses by single domain experts (necessarily incomplete) or in strategic (war) games (resource intensive). The object is to increase the analytic capability of single domain experts. Technical achievements include models that embody extensive knowledge while being transparent to users, reach back capabilities to sources to enable further analysis, and dynamic updating of variables. The team has chosen relevant research questions, designed integrated models using the systems dynamics tool STELLA and partnered with another research team to develop an interactive wiki to provide reach back and variable updates.

In the project's two years, research has developed two types of models. The first model is biofuels and food security with feedback to government policy (one model for India). This model uses knowledge from MiniCAM, EPIC, and VRIM. The second is a governance model for adaptive capacity for climate change (for India, Pakistan, and Bangladesh). These models use knowledge from VRIM coupled with information about government priorities (as described below) and variables from the World Bank on government effectiveness and corruption control.

The team worked with modelers to establish a structure and methodology for integrating data. The research team also worked with the knowledge encapsulation framework (KEF) project team to develop a wiki, comprising both research data (quantitative and qualitative largely from print sources, annotated to highlight important material) and social media (blogs and websites) related to climate change, national security, and the India-Pakistan-Bangladesh region. The two teams established a use case for KEF. Project team members contributed the KEF sources used to identify and define governance characteristics in constructing the new model. From sources, researchers identified 10 government priorities: economic growth, sovereignty, world power status, food security, energy production, water availability, poverty reduction, education, environment, and health. The researchers gave each one a weight indicating how strong a priority it is for the central government. The wiki links to the sources used to determine the weights. Using the resources of the wiki created by the KEF project, the project team continued to develop a mechanism for using social data harvested from the internet to update variables and variable values and to provide easy links to the sources for variable values. The team also established a gaming concept for the biofuels and food security model, including a narrative, player definitions, and an evaluation protocol.

Future outreach activities include papers for peer reviewed journals, conference presentations, and model demonstrations.

Engineering and Manufacturing Processes

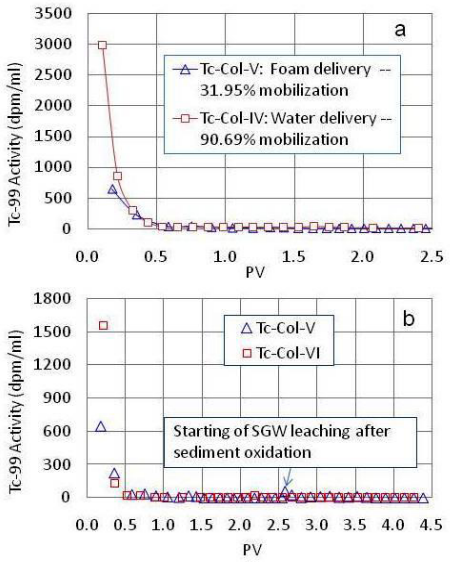
Delivery of Calcium Polysulfide to Hanford Deep Vadose Zone for Cr(VI)/Tc-99 Remediation

Lirong Zhong, James E. Szecsody

◆ This project is aimed at developing foam delivery technology for efficient, low water content distribution of remedial amendment (calcium polysulfide [CPS]) to the Hanford Site deep vadose zone for in situ immobilization of hexavalent chromium [Cr(VI)] and technetium (Tc)-99. ◆

The remediation of Cr(VI) and Tc-99 contamination in the Hanford Site vadose zone is a critical need. Water based remedial amendments delivery to the deep vadose zone faces significant technical challenges, such as spreading of mobile contaminants from the zone to the aquifer and uneven transport. The foam aided amendment delivery approach has the potential to resolve the uneven remedial fluid distribution and contaminant mobilization/ spreading issues. The objectives of the project were to investigate the retardation of remedial amendment in sediments during foam delivery and the processes controlling in situ immobilization of Tc-99 by foam delivered CPS and to study the reoxidation/remobilization of immobilized Tc-99 from the vadose zone sediment.

In FY 2008, a series of batch and column experiments were conducted to achieve the project goals. Batch tests were conducted to select the foam generating CPS surfactant solutions, determine solution foamability and reduce potential of CPS containing foams, and study the influence of foam quality, surfactant concentration, and CPS concentration on foam stability. Column experiments were performed to test CPS foam delivery to sediments (under conditions similar to the field vadose zone), to study the foam transport and interaction with sediments, and to determine the extent of Cr(VI) immobilization using this novel delivery approach. Mathematical simulation studies on foam flow in porous media were also performed. CPS containing foams with high reducing potential were prepared based on batch tests. Foam stability decreased when foam quality (ratio of gas volume to total foam volume) increased and when CPS concentration in foaming solution increased.



Effluent Tc-99 activity in column tests: a) comparison of mobilized Tc-99 between tests using water (Tc-Col-IV) and foam (Tc-Col-V) delivered CPS for immobilization and b) remobilization of Tc-99 by infiltrating synthetic ground water after treated sediment was oxidized (Tc-Col-V) by flushing 3000 PV air through column versus no oxidization (Tc-Col-VI).

For FY 2009, surfactant STEOL CS-330 was used as the foaming agent, with CPS and phosphate as amendments. Column experiments were focused on observing foam injection pressure and distribution in sediment, studying phosphate amendment transport and surfactant distribution in foam delivery, and studying Tc-99 immobilization by foam delivered CPS and reoxidation and remobilization from treated sediments during synthetic ground water infiltration after treatment.

Foam quality (percentage of gas volume in total foam volume) between 95 and 99 percent was tested to study its influence on foam injection pressure. It was observed that the injection pressure decreased with increasing foam quality. The pressure was distributed linearly through the sediment section occupied by foam flow (from the foam front to injection inlet). The pressure drop within the sediment section ahead of the foam front was small. Foam bubbles rupture at the foam-flow-front in unsaturated sediments. The result of this process is that the front of the gas injected with foam traveled significantly faster than the foam front observed in the sediment. In the column test, the retardation factor of the foam front relative to the gas front was 8.4.

In foam delivery of phosphate column tests, the transport of phosphate was retarded slightly compared with the foam front and to the distribution of surfactant in the sediment. The profile of pore water electric conductivity was similar to the phosphate distribution profile. The foam front is fairly steep and is controlled by surfactant concentration. When surfactant concentration decreases, bubbles do not reform. Also, native pore water is pushed ahead of the foam front. Foams generated from 0.5 wt% STEOL CS-330 surfactant solution at quality of 98 percent was used to deliver CPS to sediment in columns for reductive immobilization of Tc-99. The foaming solution contained 5 wt% of calcium polysulfide. Using the foam delivered calcium polysulfide, between 36 and 68 percent of the total Tc-99 in the contaminated sediment was immobilized, while less than 10 percent of total Tc-99 was immobilized when the 5 wt% CPS was delivered by water. Only 3.61 percent of the immobilized Tc-99 was remobilized by infiltrating 6 pore volumes of ground water after 3000 pore volumes of air was flushed through the treated column.

Demonstration of On-Line Monitoring and Physics Based Prognostics

Kyle J. Bunch, Pradeep Ramuhalli, Mukul Dixit, Jeffrey W. Griffin, Leonard J. Bond

◆ This project will investigate innovative sensing technologies and prognostic methods to support residual life predictions for materials subjected to stressors. The resulting capability will form the basis for advanced diagnostics and prognostics tools needed to support U.S. nuclear power plant "life beyond 60" and provide novel on-line monitoring tools for incorporation in new advanced nuclear power plants. The methods proposed will contribute to maintaining and potentially improving the safe and economic long-term operation of legacy plants. ◆

Studies presented at several recent technical conferences have indicated that material aging due to stresses and irradiation is a critical element in the failure of components in legacy nuclear power plants. Detection of early stage damage in materials is therefore important in proactive or prognostic-based life management of legacy nuclear power plants. Sometimes referred to as "condition-based maintenance," this strategy can potentially improve safety and reduce costs by detecting damage and scheduling appropriate maintenance/mitigation strategies early in the component lifecycle. Research activities in this project will be conducted within this framework. The objectives of this project are to develop online nondestructive monitoring methods to assess the condition of materials used in legacy nuclear power plants and prognostics algorithms that utilize the measurements to estimate remaining useful life.

The activities undertaken in this project seek to establish the science and technology base for early detection of some classes of damage encountered in aging nuclear power plants, and provide a first demonstration of the integration of damage characterization to a prognostic (estimate for remaining life) applied to a nuclear power plant system. To this end, nondestructive evaluation (NDE) technology for online monitoring will be developed using simulation and experimental studies. These studies will characterize detection sensitivity of the NDE method(s) to early stage damage. Measurements on laboratory and service degraded specimens will be used, with probabilistic fracture mechanics principles, to develop and validate prognostics algorithms for estimating remaining useful life.

Early damage in stainless steel and nickel-based super-alloys results in changes in their electrical and magnetic properties. Therefore, the research focus for FY 2009 was on developing nondestructive (i.e., without destroying the utility of the specimen) low frequency electromagnetic measurement methods sensitive to these changes. The methods selected for evaluation were the multi-frequency eddy current and magnetic Barkhausen noise measurements. In order to determine the sensitivity and selectivity of these techniques to early-stage damage, parametric studies using finite element simulation models were conducted. Simultaneously, multiple specimens with different levels of damage were prepared for collecting experimental data, and validating the models. An experimental setup was designed for obtaining the nondestructive measurements on these specimens, and data to date indicate good correlation with early stage damage. In addition, PNNL received specimens with different levels of fatigue damage through an International Atomic Energy Agency coordinated research program on advanced diagnostics. The damage mechanisms in these samples are complementary to those created under this project. Nondestructive inspection of these samples using the eddy current method was also performed, and preliminary analysis of the data again indicates good correlation with damage level.

Prognostics algorithms require an estimate of the current state of the material, along with a model describing the evolution of damage over time. Given the uncertainties inherent in estimating environmental stressor levels over time and in estimating the current material state due to measurement noise, a probabilistic model of damage evolution is necessary. Three distinct algorithms for prognostics have been identified, with implementation and testing underway.

We also focused on fundamental studies on electromagnetic nondestructive measurement sensitivity through simulation and experiments. During FY 2010, the focus will be on integrating the nondestructive inspection with the prognostics algorithms to obtain estimates of remaining useful life. In addition to the electromagnetic measurement methods explored in FY 2009, additional experiments using acoustic measurement methods will be conducted on the specimens. These data will result in information about the state of the material that is orthogonal to that obtained from the electromagnetic measurements. Both sets of data will be used to generate a database of measurements correlated with the level of damage (or equivalently the remaining useful life of the material). Along with the prognostics algorithms that have been identified, this database will be used to provide a demonstration of the integration of damage characterization to a prognostic (estimate for remaining useful life).

Development of a Ballistic Electron Microfabricated Cathode

Kyle J. Bunch, Laxmikant V. Saraf, Hong (Amy) Qiao

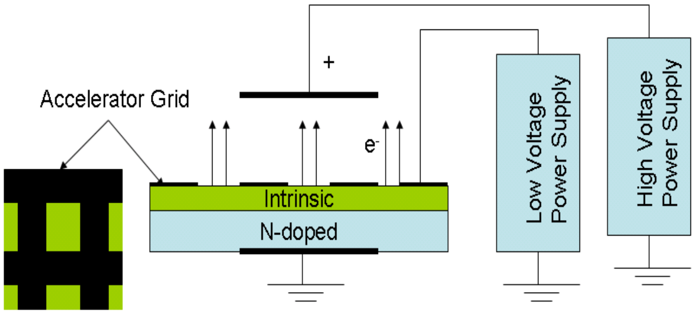
◆ A solid-state cathode with a high emission density will serve as an enabling technology for many different applications, including high contrast flat panel displays, conventional vacuum microwave/mm wave devices, or next generation vacuum microelectronic devices. ◆

Cathode technology is used in applications including high powered microwave amplifiers, oscillators, pulsed power, and potentially next-generation flat panel displays. Conventional cathodes rely on thermionic emission of electrons from a material surface and have the disadvantages of short lifetimes, difficulty in miniaturization, and heat dissipation issues. Research over the last 30 years has focused on replacing thermionic cathodes with field emission tips in which electrons are stripped from the surface of a material using a high voltage field gradient applied to the surface of the tips. This approach has met with difficulties including poor emission densities as well as tip degradation due to the electron current. This research involves exploiting the advances in the processing and deposition of materials, especially diamond and diamond-like materials in order to create a cathode that directly accelerates electrons within an intrinsic material region and into a vacuum. The potential advantages of this approach include high current densities, long cathode lifetimes, and compatibility with microfabrication processing methods. Such a solid state cathode would represent an enabling technology, leading to novel devices combining vacuum electronics with solid state electronics.

During FY 2008, we selected three materials as promising: diamond n-doped silicon, silicon carbide, and gallium arsenide. These material have a combination of high breakdown field strength, long electron mean free path (for ballistic transport), and practicality for use with current microfabrication methods, and they are the most promising materials found for the creation of a solid state, ballistic-electron cathode.

In FY 2009, we focused on three areas of progress: simulation, fabrication, and testing. Field simulations were performed using COMSOL electromagnetics, a commercially available finite element simulator. Results show that field emission on the order of 1 A/cm^2 is possible from a diamond surface. This simulation looks at electrons accelerating within the diamond intrinsic region and overcoming the work function of the diamond surface. While the electron densities are promising (a conventional thermionic cathode is 10 A/cm^2), the use of an accelerator grid should increase these electron emission density significantly. An acceleration (or control) grid applies a large electric field gradient across the intrinsic region (undoped diamond or silicon carbide). An n-doped substrate serves as a source of electrons to inject into the intrinsic accelerator region. An external plate serves to collect and measure the emitted electrons.

The selection of suitable accelerator material considered a combination of criteria including the material voltage breakdown strength and its suitability for integration within existing semiconductor materials. Two sets of wafers were produced: 0.2 μm intrinsic chemical vapor deposition diamond on n-doped silicon, and 0.2 μm intrinsic silicon carbide on n-doped silicon carbide. The latter was chosen for its high breakdown strength and its commercial availability. Surface grids were fabricated on the surface of these wafers, and they are ready for emission testing. The grids are composed of platinum deposited using chemical vapor deposition. Also completed was the vacuum chamber and apparatus needed for emission experiments on the sample devices. As configured, the vacuum chamber will allow for testing of the ballistic cathode concept. A low voltage is applied to the accelerator grid to inject electrons from the n-doped material into the intrinsic accelerator region (diamond or silicon carbide). The electrons not intercepted by the grid are accelerated into vacuum and collected by the high voltage power supply. Currently, this setup is ready for testing once the configuration is approved and personnel have met current safety training requirements.



The setup for emission testing of current devices.

Simulations have shown the ballistic electron cathode concept to be a viable means for creating a solid state cathode. Several configurations of the cathode have been manufactured, and acceleration grids have been deposited using platinum for the conducting metal. The most promising materials (diamond and silicon carbide) are being used for the acceleration layer. Testing of the cathode devices will be performed in FY 2010.

Optimizing Generation Portfolios and Dispatches with Consideration of Environmental Constraints in View of Significant Penetration of Intermittent Renewable Energy Resources

Yuri V. Makarov, Shuai Lu

◆ This project investigates intermittent renewable generation on operating cost, wear and tear, emissions, and other environmental impacts of conventional dispatchable generators and develops key elements of a new coordinated approach to minimize these impacts, including optimizing generation portfolios and dispatch procedures. Staff expertise and the new methodology developed in this project will build capability to support key issues, including reducing the environmental impacts from energy production/use and cost effectively improving the energy efficiency of the U.S. economy. ◆

With enhanced wind power generation to certain levels, a significant increase of hour balancing power capacity is required, as well as of the number and size of movements on generators' hourly schedule and cycling (i.e., the number of starts and stops). Uncoordinated integration of intermittent resources could reduce the efficiency of dispatchable units, cause additional wear and tear, increase SO_2 and NO_x emissions from thermal units, and cause more fish problems at hydropower plants.

This project develops approaches to evaluate the impacts described above and develops key elements of a coordinated approach to minimize these impacts. A software platform is currently under construction that can simulate the operation processes in a power system and have generator models capable of assessing the cost attributable to frequent movements and environmental impacts. The platform will then be used to test the potential solutions mitigating those impacts, including optimizing the mix for the new generation additions, use of energy storage and grid responsive load, and the development of better unit commitment and dispatch strategies. Industrial support and contacts with the Bonneville Power Administration, California Independent System Operator, and Calpine already gained in this project create a basis for future commercialization of the project results.

The project has two phases. During FY 2008, we formed the knowledge foundation for the proposed work by surveying relevant government policies and literatures, and collecting information from industries including generation companies and transmission system operators. We developed the framework of a power system operation process simulation program to evaluate the impacts of intermittent resources on power system operations. This framework is now being used by DOE and the Bonneville Power Administration to evaluate production cost, emissions, control performance, and related items with various wind integration scenarios.

We also completed a prototype program in Matlab for the unit commitment process with generation flexibility constraints. We proposed this process as a solution to solving the increasing difficulty with system real-time balancing processes. We developed the formula to calculate the costs and emission rates for fossil fueled power plants associated with varying level of output caused by accommodating intermittent resources. The formulas will be used with emission allowances to represent emission constraints in the unit commitment problem. Environmental limitations with hydro projects were summarized, and the representation of these limitations was formulated as constraints in the unit commitment problem.

Based on the progression of the project, we proposed a new framework for the unit commitment process. This framework incorporates the generation flexibility requirements, emission constraints for thermal generators, and environmental constraints for hydro projects into the existing unit commitment algorithm. A paper describing this framework was submitted to the 2010 Wind Power conference that showed examples of how the proposed flexibility constraints could reduce risks with real-time operation and the occurrences of extremely high or negative energy prices on the spot market. Unit commitment under this new framework will be critical to the economic and reliable operation of the power grid and minimization of the negative environmental impacts, especially when high penetration levels of intermittent resources are approached, required by renewable portfolio standards in many states.

We anticipate that our coordinated framework will help meet the goals and develop balanced states' renewable portfolio standards, plan and optimize new generation additions at the State Public Utilities Commissions, provide environmentally friendly unit commitment, and dispatch patterns posing minimum stress on the other units at the Utilities and Control Area Operators, and develop plans for integrating more balancing resources such as buildings that interact intelligently with the grid, integrated distributed power resources, and energy storage.

Process Modeling of Chemically Complex Solid-Liquid Suspensions

David R. Rector, Mark L. Stewart, Adam P. Poloski

◆ The design and construction of successful chemical processing systems depend heavily on the ability to scale fundamental processes developed during bench- and pilot-scale testing. Our objective is to develop a general simulation capability to predict the performance of chemically complex multiphase chemical processes for a wide range of applications. ◆

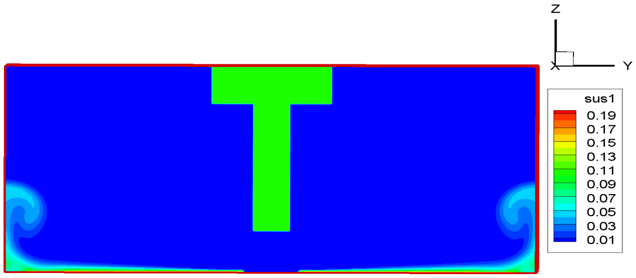
Many examples exist in the chemical processing industry that illustrate the difficulty of chemical process scale-up from benchtop or pilot-scale experiments, including high-level waste treatment. Current simulation methods use assumptions and approximations to fit the existing computational methods and resources. These assumptions can result in poor scaling predictions. Our objective is to develop and demonstrate a general simulation capability to predict chemical process performance that uses highly parallel computational resources to reduce assumptions and approximations. Physical models are incorporated that are appropriate for specific applications; the method is being validated using available data. The simulation approach used in the ParaFlow computer program is based on the lattice kinetics methods. Distribution functions containing information about the pressure tensor streams to adjacent lattice sites, and the summation of these quantities results in equations solved for mass, momentum, and scalar transport. The method depends only on local information and scales nearly linear with the number of computer processors.

In FY 2008, we incorporated solid-liquid multiphase flow models for the sediment and suspended solids. The sediment is modeled using a phase field representation, where the phase interface embodies a continuous order parameter profile that moves smoothly through the computational grid. The sediment bed changes through deposition by hindered settling and erosion when the surface shear stress exceeds a specified yield stress. A dynamic lithostatic model was included where the internal stresses are calculated and sediment can flow when a yield stress is exceeded.

The transport equation for suspended solids includes convection, hindered settling, diffusion, and turbulent mixing. In addition, the solid particles in sheared suspensions migrate in the direction of the gradient to higher velocity regions. The irreversible particle collisions that occur in a sheared suspension result in fluid (normal) stresses that result in secondary flows behavior. A series of simulations were performed to determine the flow verses pressure drop behavior of suspension transport pipelines. Comparison of simulation results with experimental data showed very good agreement.

During FY 2009, we developed additional capabilities for ParaFlow. A hierarchal grid structure was incorporated that allows computational nodes to be subdivided into regions where additional detail is desired. The time step is also subdivided to maintain the same Courant number, plus this capability is used to focus computational resources where they are most needed in a simulation. Many environmental and energy flow applications, including dissolution and precipitation, involve chemical reactions; for this reason, a thermodynamically based chemical reaction model was added. The solution method used is a Gibbs free energy minimization scheme that is especially useful for systems with high ionic concentrations. Testing and optimization of the method is in progress. The existing Reynolds-Averaged Navier-Stokes model has limited accuracy for certain applications; thus, a large eddy simulation turbulence model has been incorporated and tested. Work continues on developing initial and boundary conditions and examination of hybrid schemes.

A series of application simulations were also performed in FY 2009 to demonstrate ParaFlow capabilities: 1) the flow and heat transfer in a section of a 19 pin LMFBR fuel bundle was simulated to determine the effectiveness of wire wrap induced mixing on temperature distribution, 2) a continuum model was developed for a catalyst bed reactor downstream from a coal gasification unit using effective flow resistance/reaction rates to determine the effect of sulfur poisoning as a function of time. Discreet particle bed simulations will determine effective parameters more accurately, 3) a series of simulation studies were performed to optimize flow models for the applications, as many environmental applications involve suspension of solids in liquids using jet pumps and pulse jets, and 4) a model was developed for a pulse jet mixing tank. Preliminary simulations were performed on the transient's initial portion.



Simulation of solid particulate resuspension using a pulse jet mixer.

Activities scheduled for FY 2010 include simulation of filters used in leaching processes and completion of pulse jet mixing tank simulations.

Materials Science and Technology

Accelerated Fuel-Cladding Test Methods and Tools

Charles H. Henager Jr., Charles F. Windisch Jr., Shenyang Hu, Howard L. Heinisch Jr.

◆ Innovative experimental tools and techniques and computational models are required to accelerate fuels and materials qualification for advanced nuclear reactors in order to reduce testing costs and to save development time. This study will develop miniature and subminiature specimens to understand and predict fuel-cladding interactions for advanced nuclear reactors and for new fuel forms. ◆

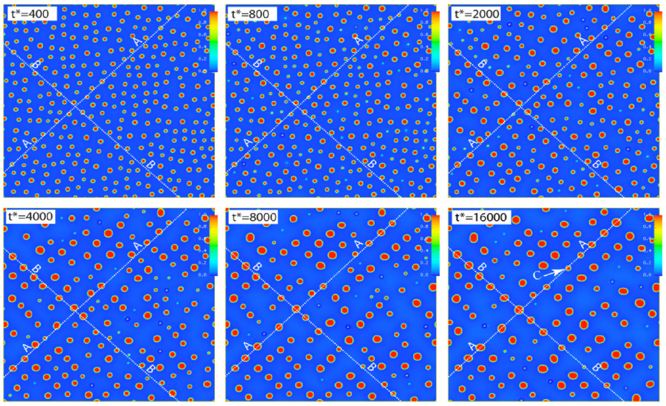
The Global Nuclear Energy Partnership (GNEP) was created to help the United States and the world address spent nuclear fuel, nuclear proliferation issues, and advanced nuclear energy sources. One goal of the GNEP is to build a fleet of advanced sodium-cooled burner reactors to transmute transuranic elements to reduce waste storage and minimize proliferation concerns associated with spent fuel. This will require development and qualification of new actinide fuels. For successful advanced reactor development, innovative approaches are necessary to reduce the fuel qualification time by 30 to 50 percent using a combination of innovative experimental tools and techniques with appropriate modeling.

This research addresses the need for simulation of fuels and fuel-cladding materials for advanced reactors by addressing the problem of accelerating fuel qualification with innovative test specimen design, in situ testing, and computational modeling. We developed miniature and subminiature specimens to understand fuel-cladding interactions for advanced reactors and for new fuel forms. The specimens were designed to evaluate transport of mobile species from advanced fuel mixtures while allowing chemical and mechanical test data to be obtained during accelerated thermal or radiation exposure from ion beams or neutron radiation.

During FY 2007, our main accomplishment was that a laser Raman accelerated kinetic tool was demonstrated using alloy HT-9 in the form of 3 mm diameter disks. We observed complex oxidation kinetics at elevated temperature and identified all phases formed during the test in only 6 hours at 700°C. The small disks were then coated with a surrogate fuel coating and key differences in overall kinetics were identified and measured. Miniature specimen mechanical property testing was begun using the same 3 mm diameter disks used for the oxidation studies. The modeling task began to discuss ion irradiations, and differences between high-energy ions and neutrons were been outlined. We also completed collecting irradiation experimental design tools but were not previously centralized. For FY 2008, miniature tensile specimens of HT-9 fast flux test facility heat alloy were again fabricated and tested at elevated temperature in air. Additionally, a new phase field model of prototypical nuclear fuel gas bubble microstructure and thermal conductivity evolution was developed.

Primary accomplishments during FY 2009 were once again demonstrating a laser Raman method for 3 mm disks using alloy HT-9 coated with fuel and fission product surrogates in the form of 3 mm diameter disks and initiating a new process to modeling radiation damage evolution using a modified phase field approach. The laser Raman studies developed a kinetic signature using 3 mm disks of alloy HT-9 coated with zirconia (a surrogate for UO_2) and zirconia plus Ga (as a fission product surrogate) using sputter deposition. The samples were then subsequently oxidized in air for up to 8 hours at 650°C. Coupled with x-ray photoelectron spectroscopy depth-dependent chemistry data, our laser Raman data distinguished clearly between uncoated HT-9 and coated variants. The Ga-doped zirconia exhibited different oxidation kinetics compared to the zirconia-coated HT-9. This is significant because alloy HT-9 is one of the preferred alloys for advanced fuel cladding material. Two papers were published in the *Journal of Nuclear Materials* discussing this data and the methodology.

The modeling task developed a new phase field model for microstructural evolution of nuclear fuel and other materials. Based on the success of this approach, we further developed the method to model a void lattice in materials using a new approach to radiation damage modeling. Vacancies and self-interstitial atoms (SIAs) were included in the model along with a solid phase and a void phase. It was demonstrated that a void lattice is stable under the assumption of directional SIA motion similar to what has been determined using other methods, such as kinetic Monte Carlo methods.



Temporal evolution of a void ensemble for the case with migration rate of SIAs equal to 104 times faster than vacancies and along <110>-type directions. The majority of the area denotes the metal matrix with low vacancy concentration, while the "ringed" portions indicate voids with high vacancy concentration.

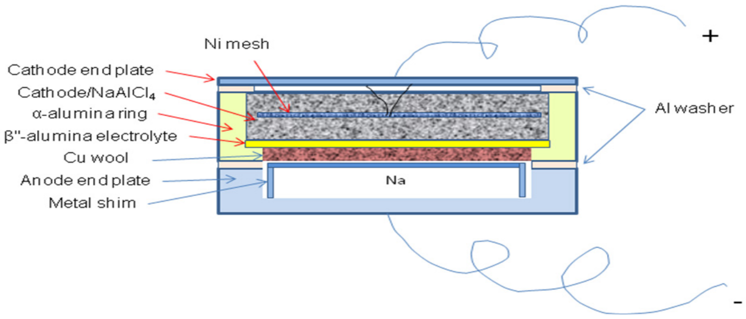
Advanced Cathodes for Sodium-Beta Batteries and Renewable Energy Applications

Z. Gary Yang, Xiaochuan Lu, Gordon Xia, John P. Lemmon

◆ With current compositions chemically corrosive, unsafe, or too expensive, the cathode needs improvement in electrochemical activity. To address these issues, we developed novel structures and new chemistries that can demonstrate satisfactory performance at a cost savings. This research is integral to build capabilities around developing economic Na beta battery modules based on planar designs for storage of electricity from renewable sources. ◆

Growing environmental concerns about the use of fossil fuels and their resource constraints, along with the current trend of monetization, have led to aggressive portfolios in renewable energy from solar and wind sources. To make effective use of and dispatch the intermittent renewable demands the creation of storage for electrical energy. The same technologies are also increasingly needed to improve the reliability and efficiency of the Nation's electrical grid to meet the growing demand for high quality electricity. Among the most promising storage technologies are Na beta batteries capable of a module design and a storage capacity up to MWhs. However, current Na beta batteries are not yet technically viable and economically feasible for the important applications.

The following describes progress during FY 2009.



Schematic of the single cell construction.

Cathode/Cell Development. A halide based cathode has been developed and successfully tested in single cells. The cathodes were fabricated from a power mixture of 58.4 wt% Ni, 31.8 wt% NaCl, and 9.8 wt% pore former with NH_4HCO_3 added as a binder. The mixtures were thoroughly mixed, pelletized, and fired at 700°C under a flowing atmosphere of Ar + 2.75 % H_2 for 1 h. During fabrication, Ni wire was imbedded into the cathode powders as current collector. To evaluate the electrochemical performance of cathodes, β" alumina electrolyte discs were fabricated via the vapor phase process and assembled into cells with the aforementioned cathodes. A new approach was developed to make the electrolyte and cells, starting with high purity α alumina and Yttria stabilized zirconia. The mixture of 70 vol% α alumina and 30 vol% Yttria stabilized zirconia were ball milled, dried, and sieved before being combined with dispersant and solvents in a certain ratio and milled for 24 h. Plasticizer and binder were added into the solution and milled for another 24 h. After lamination, the sheet was punched into circular discs fired at 1600°C to achieve a full density (above 99 percent). The samples were creep flattened and ready for converted to β" alumina. During conversion, the α alumina/Yttria stabilized zirconia discs were packed in a powder bed of β" alumina (prepared separately) and heat treated at 1450°C in the air for a designated period of time. The conversion occurs by a coupled transport of sodium and oxygen ions from the packing β" alumina powders to the samples. Varied thickness (200 to 700 μm) electrolytes and cells were fabricated for evaluation.

Cell Construction and Evaluation. To evaluate the cathodes and cells, a cell test setup was built (refer to figure). The converted β" alumina disc with the diameter of 21 mm was glass sealed to an outer thicker α alumina ring. A thin layer of lead was coated onto the anode side of the electrolyte to improve the initial sodium wettability. The cell assembly was then moved into a glove box. The Ni/NaCl pellet was placed in a cathode compartment of the cell and impregnated with molten $NaAlCl_4$ electrolyte at 300°C on a hot plate. A metal shim was inserted into the cavity of the anode end plate. A small amount of sodium metal along with a copper wool filled the gap between the electrolyte and shim. The anode and cathode end plates were then compressed to the α alumina ring with the help of alumina washers. The aforementioned procedure is indeed a novel approach that has proven effective in sealing alumina electrolyte and metal parts. Platinum leads were welded to the electrode end plates as current collector. The effective cell area was 1.84 cm^2, the assembled cell was placed in a furnace inside the glove box, and cell testing was carried out using an electrochemical interface from 350 to 250°C. A constant current mode was used during charge/discharge processes.

Our work has established new capabilities in Na beta alumina cell fabrication and evaluation. Halide-based cathodes were developed and tested. Importantly, our preliminary work improved the feasibility of planar designs constructed from halide based cathodes. The effect of certain chemical additives toward the cathode and single cell performance will be evaluated in FY 2010.

Advanced Materials for Capturing Lanthanides and Transition Metals from Fission Products

Wassana Yantasee, Glen E. Fryxell, Mychailo B. Toloczko, R. Shane Addleman

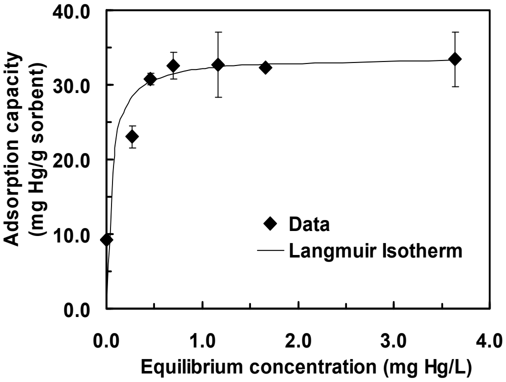
◆ This project seeks to develop and evaluate advanced materials for the selective capture of specific decay species such as might be encountered in spent nuclear fuel or waste from human blood, dialysate, high acid solutions, and natural waters. The successful development of sorbent materials for these species in the challenging matrices will enable not only their collection and separation from nuclear wastes and natural waters but also their monitoring and treatment strategies of the workers at DOE sites. ◆

The goal of this project is to develop and evaluate new sorbent materials for lanthanides and transition metals for various specific needs. Four classes of functional materials (mesoporous silica, mesoporous carbons, activated carbon, and magnetic nanoparticles) have been successfully developed at PNNL for the capture of heavy metals, actinides, lanthanides, and transition metals in the aqueous phase. The removal of lanthanides and transition metals from challenging matrices (e.g., human blood, high acid solutions, dialysate, and natural waters) have not been investigated and thus will be the focus of this work.

Seven organically modified mesoporous silica (SAMMS) were made and tested for lanthanide capture (La, Ce, Pr, Nd, Eu, Gd, and Lu) in nitric acid, hydrochloric acid, river water, ground water, and seawater. Ligands included the hydroxypyridinones, various chelating phosphonates, and various glycine derivatives. In addition, a templated mesoporous carbon built around the 1,10-phenanthroline ligand (for transition metals) and a chemically modified activated carbon decorated with thiol groups (for "soft" heavy metals) were also made. Tests were carried out to determine metal ion binding kinetics and binding affinity as a function of pH, matrix, competing ions, and similar materials. For the lanthanides, all SAMMS sorbents studied were found to have good affinity for the lanthanides. The best ligands were found to be the 1,2-hydroxypyridinones and the various phosphonic acids (Ac-Phos and diphos).

Functional mesoporous carbon made from the 1,10-phenanthroline building block (Phen-FMC) was also found to be a very effective method for capturing transition metal ions. The pK_a of the protonated 1,10-phen ligand is about 5, indicating that it exists as the corresponding ammonium salt at lower pHs. This cationic species was found to be an effective anion exchange material, with Kds in excess of 1,000,000 for $PdCl_4^{-2}$ at pHs below 4. At pHs above 5, the 1,10-phen ligand is neutral and an excellent metal chelator. Under these conditions, Phen-FMC was found to bind effectively to first row transition metal cations (e.g., Co, Ni, Cu, Zn) with Kds commonly in excess of 300,000. Sorption kinetics were rapid, with greater than 99 percent of the Co captured from solution in less than 30 min. Phen-FMC was also found to bind Co and Ni in plasma as well as being more effective than either Chelex 100 or activated carbon in these applications. Binding of the second row transition metal cations was variable, being good for Pd but poor for Rh (ligand exchange rates for this cation appear to be quite slow).

In an effort to capture the "softer" second and third row transition metal cations, a novel sorbent was designed and built by decorating an activated carbon framework with thiol groups. This sorbent ($AC-CH_2-SH$) had a specific surface area of 1244 m^2/g, a pore volume of 1.29 cc/g, and 0.65 mmole of thiol/g of sorbent. Binding affinity for Hg(II) was exceptional across the entire pH range studied (from 0.2 to 8.5), with Kd values well in excess of 1,000,000. At more moderate pHs, $AC-CH_2-SH$ was also effective at binding Pb, Ag, Cd and Cu. Hg sorption kinetics were quite rapid, with a 1000 ppb Hg solution knocked down to 0.04 ppb in less than 30 min (significantly faster than the currently used commercial sorbents like GT-73 and sulfur impregnated activated carbon). Isotherm data revealed a mercury capacity of 33 mg/g.



Absorption capacity isotherm for Hg onto $AC-CH_2-SH$ at a pH of approximately 5.5.

The development and evaluation of sorbents for lanthanides and transition metals was explored in some detail in FY 2009. For FY 2010, we will design and synthesize novel sorbent materials to perform these separations and also perform a proof-of-concept chromatographic separation of lanthanides using these novel nanoporous sorbents. This work is anticipated to provide the foundation for a proposal aimed at developing a novel separation method for lanthanides.

Advanced Nuclear Magnetic Resonance Characterization of Energy Storage Materials

Jianzhi Hu, Li-Qiong Wang, Vijayakumar Murugesan

◆ This research will provide new insights into the physicochemical phenomena that underlie the operation of lithium (Li)-ion batteries, particularly the ion transport mechanisms and chemical status. This is especially important for development of new nano-structured electrode materials, which are expected to lead to improved energy and power densities and improved long-term stability for electrochemical energy storage systems. ◆

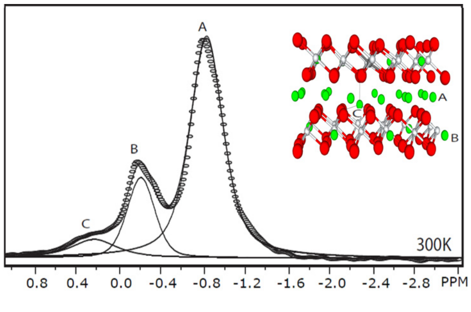
Developing advanced energy storage materials for emerging applications such as plug-in hybrid vehicles or the efficient use of renewable energies are critical enabling technologies. Although Li-ion batteries have gained commercial success for mobile electrics applications, they do not meet requirements for emerging, large-scale applications in terms of energy/power density, life, safety, and cost. Fundamental improvements to electrochemical storage performance are required for emerging applications in transportation and electricity production. To reach this goal, a molecular-level understanding of the detailed ion transport mechanisms is critical for designing Li-ion batteries with significantly improved performance.

We propose to apply our unique capabilities in high field nuclear magnetic resonance (NMR), including application of low to moderate field range combined with our unique hyperpolarized ^{129}Xe spectroscopy and development of unique high resolution in situ capabilities, to study ion transport mechanisms and status, thereby providing a complement to ongoing diagnostic studies using synchrotron techniques, vibrational spectroscopies, electron microscopy, and magnetic resonance. We will investigate the Li-ion battery, particularly the nano-structured TiO_2 electrode materials. In addition, we will launch studies on high capacity SnO_2 based anode materials and high surface area mesoporous Si/C composites/nanowires. The methods and technologies established in this project are applicable to a wide range of energy storage materials, including other batteries such as proton, supper capacitors, hydrogen storage materials, and proton membranes.

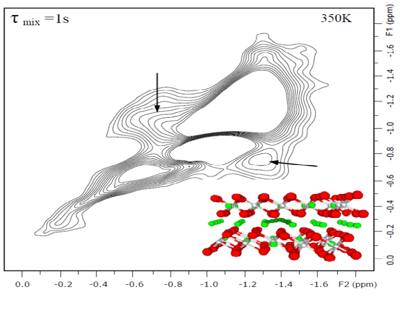
The transition metal oxides with tunnel or framework structures have been widely investigated as electrode materials. Among the various transition metal oxides, Li inserted titanium dioxide (TiO_2) based materials (Li titanate) is a promising candidate for anode material due to its low production cost, low environmental impact, and high capacity. In order to clarify the structural evolution of nano-structured rutile and anatase type TiO_2, we carried out NMR spectroscopy, x-ray diffraction, transmission electron microscopy, and density functional theory studies. These studies reveal that the host rutile nanorod holds Li insertion only up to 0.12 Li/TiO_2 (x=0.12) without significant changes in either nanorod morphology or structure. Further Li insertion (x~0.5) induces a structural transition from rutile to spinel type structure ($Fd\bar{3}m$) and to rocksalt type structure ($Fm\bar{3}m$) at x~0.95. These consecutive phase transition during Li insertion in nano-structured TiO_2 could cause battery degradation during electrochemical cycles; hence, fully phase transformed Li titanate material rather than pure TiO_2 might provide more stable reversible capacity.

The Li jump rates were determined using ^{7}Li stimulated echo experiments and showed very slow Li diffusion (i.e., 60 Hz at 350 K). This partial and slow Li diffusion process is limited by the availability of nearby vacancies. Using high field ^{6}Li MAS NMR, a new tetrahedral Li occupation has been detected, along with the three crystallographic octahedral sites in the monoclinic Li_2TiO_3 corroborated by molecular dynamic simulations. The Li diffusion pathways were obtained employing ^{6}Li two-dimensional exchange NMR, which clearly indicates that Li diffusion along the c axis. Combining ^{6,7}Li NMR results and molecular dynamic simulations, Li conduction in monoclinic Li_2TiO_3 is three-dimensional, provided suitable nearby vacancies are available.

During FY 2010, we will perform a comprehensive H-1 and V-51 NMR investigation on redox chemistry associated with the all vanadium redox flow battery. We will continue our ex situ and begin full-scale in situ applications and determine the best method of performing the in situ detection.



^{6}Li chemical shift (ppm)



^{6}Li 2D exchange spectra of monoclinic Li_2TiO_3

Advanced Sorptive and Signature Indicating Materials for Ultra-Trace Proliferation Detection

Jay W. Grate, R. Shane Addleman, Keith D. Miller, Praveen K. Thallapally, Jon M. Schwantes,
Richard M. Ozanich, Marvin G. Warner

◆ The collecting, enhancing, and detecting signatures of undeclared nuclear activity from extremely dilute environmental samples taken at a distance from nuclear sites are essential technical capabilities addressing the risk of nuclear proliferation. ◆

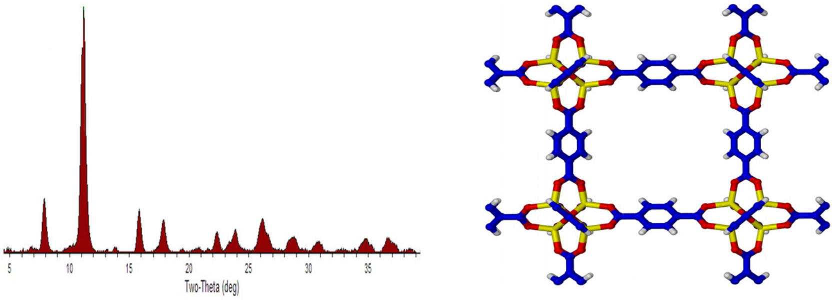
Signatures for nuclear proliferation can occur in the gas phase as gaseous molecules or aerosol particles, in the liquid phase as dissolved ions, or as residues or components of solid samples. This project will develop three different but complementary technologies for concentrating and detecting signatures of activities that could be associated with nuclear weapons proliferation.

Metal Organic Frameworks for Noble Gas Sorption. With regard to the gas phase, the collection of noble gases is an important aspect of monitoring and detection of undeclared nuclear activity. Sorptive materials play a key role in this collection. This project addresses a new type of sorbent, metal organic frameworks (MOFs), with superlative properties compared with current carbons and zeolites for gas capture and separations. We will develop and investigate metal organic framework materials for gas collection and separation of noble gases such as xenon that are produced during nuclear fission in reactors. The development of these materials will lead to more effective collection of noble gases from greater distances in the face of rising backgrounds.

Magnetically Active Sorbents for Proliferation Signature Collection and Detection. Capture of low concentration signatures from complex matrices and/or large volume samples is challenging. Magnetic nanoparticles offer a novel means to capture and pre-concentrate trace level signatures of interest selectively including radionuclides, heavy metals, and organic compounds. By functionalizing these high-surface area nanoparticles with a variety of proven chemosorbents, specific elements of interest may be targeted and preferentially extracted away from complex matrices at a capacity and selectivity greater than commercial sorbents. Once sorbed, the magnetic character of the nanoparticles allows them to be magnetically manipulated. This provides the ability to trap the functionalized nanoparticles magnetically in one geometry for a sample collection to release and retrap either for recycling purposes or prevention of clogging, biofouling, and/or placing them in a specific geometry for signature detection using a variety of measurement platforms.

Protein Based Uranium Detection. This project will significantly enhance the capability for stand-off detection of upstream uranium processing using novel protein-based fluorescent sensors that bind to uranium species. These proteins will be designed to fluoresce only in the presence of labile uranyl species and are functionally tested for high affinity/specificity to demonstrate effective and enhanced fluorescence detection. Design of the sensor material will be based on metal binding trimeric coiled coil peptides fused to circularly permuted variants of fluorescent proteins. Our research will use the green fluorescent protein (GFP) because its structural and fluorescent properties have been well characterized. However, the results can also be extended to the design of other novel metal binding fluorescent proteins.

For FY 2010, we will select and synthesize appropriate MOF candidates, characterize the physical properties of the synthesized materials to verify structure, and characterize other specific properties relevant to noble gas sorption, collection, and separation. These data will support determination of the usefulness of these new materials in national security applications. Through our continuing research, we will gain a better understanding of how to make/select, modify, and manipulate magnetic nanoparticles for trace level analyte capture from large volumes. Finally, we will design and construct novel protein structures for fluorescent sensing of uranium. The high throughput method will be used to select high affinity GFP fusion structures with the desired fluorescence sensing properties.



Powder X-ray and single crystal X-ray diffraction experiments confirms the successful synthesis of MOF-5. The solvent molecules were removed for clarity (right).

Application of Imperfection Modeling to Accelerated Fuel Clad Qualification and Characterization

Curt A. Lavender, Elizabeth V. Stephens, Stan G. Pitman, Richard W. Davies

◆ The novel imperfection modeling approach will shorten qualification time by providing a quantifiable measure of the performance of a new clad material rather than typical pass/fail outcomes based on acceptance limits. The technique uses a digital image to measure strain and describe the sample quality to predict future clad performance without costly, time-consuming in-reactor testing or extensive ex-reactor parametric studies. ◆

In-reactor fuel clad performance is sensitive to the numerous quantity and type of manufacturing defects encountered during tube fabrication and end plug welding. This sensitivity can be dependent on the clad base material and the processing method used that affects microstructure, texture, surface quality, mechanical properties, and defect population. The challenges of selecting a new material or joining method for cladding are similar to those encountered in most engineering applications. To address this issue, PNNL developed methods for rapid material and process selection with non-funded work. For example, the focus of one of these projects was on rapid qualification of advanced high strength steels and new joining methods for aluminum alloys. Through this method, new steel alloys and aluminum joining methods have been implemented into high volume automotive manufacturing with predictable performance without the normal 10-year development cycle. The purpose of this project is to apply related techniques to sample geometries and materials of specific interest to the nuclear industry.

This research has two principal advantages over conventional nuclear fuel manufacturer test methods. First, the approach uses digital image correlation to quantify the strain in real-time that develops during internal pressurization, tube expansion, and subsequent localization and fracture of fuel cladding. Second, using this approach and test samples from a given population, a quantitative statistical distribution of the fuel clad performance during internal pressurization and subsequent burst will be derived. The benefit of this statistical distribution is a probabilistic understanding of the material performance under internal pressure conditions to predict performance of a fuel cladding population, which should yield a detailed prediction of long term performance of given fuel clad material.

In FY 2008, the tube burst and digital imaging system were completed, and tubes with three heat treatments and a variant with ultrasonic test indications were evaluated. The test method was indicative of the tubing quality and produced data of interest to the Nuclear Regulatory Commission, tubing users, and manufacturers. Several key outcomes occurred using the new system: 1) uniform strain was validated as an improved method to evaluate tubing quality, 2) flawed tubes demonstrated a higher imperfection level, and 3) irrespective of heat treatment, the method predicted the same level of manufactured tubing quality.

During FY 2009, research expanded by initiating Zr-4 end joining methods and applying the modeling approach to tubes with weldments. In addition, oxide dispersion strengthened alloy clad fabrication was initiated, and work continued on the imperfection modeling development. Tube burst testing and digital imaging spectroscopy was used to determine optimum processing parameters for tungsten inert gas welded end plugs to produce a quality weldment population for evaluation. Electron beam tube weldments were also evaluated using previously developed electron beam weld processing parameters for nuclear cladding evaluations. The burst test results and uniform strain of the two weldment populations were compared to the results of acceptable 865°F annealed Zr-4 tubes.

Weibull distributions of the uniform strain data from all three populations were plotted. Although similar burst pressures were observed between the electron beam tubes with weldments and acceptable annealed tubes, different slopes are observed in the Weibull probability plot, indicating different probabilistic behaviors. This difference is more pronounced when extending the tail end of the probability plots. Higher failure rates at the same strain level are in tubes with weldments compared with annealed tubes. The weldments are inherently probabilistic, and results to date indicate this method to be a useful tool for weld qualification.

Much of FY 2010 will focus on oxide dispersion strengthened alloy processing. The coarse distribution of oxides in the material result in probabilistic structures due to the inhomogeneous microstructure formed. The coarse oxide distribution may be controlled by processing. Therefore, the imperfection modeling approach may prove useful in predicting future performance. The modeling approach will be applied to oxide dispersion strengthened cladding materials and weldments. A powder source for the cladding fabrication has been identified including manufacturing methods. In addition, continued development of the imperfection modeling approach and development of an algorithm for rapid test analysis will occur.

Biotemplated Synthesis of Encoded Bimetallic Nanoparticles

Yuehe Lin, Yongsoon Shin, Jun Wang, Zhiwen Tang

◆ This project aims to develop novel approaches to synthesize bimetallic nanoparticles with controlled architectures inside protein cavities and prepare biofunctionalized graphene for biosensors. ◆

Although protein cages have been widely investigated for synthesizing inorganic and metallic nanoparticles, bimetallic nanoparticles with controlled composition and uniform sizes remain a significant challenge. In this project, we will focus on bimetallic nanoparticle formation: how solution and protein chemistries affect diffusion of metal ions into the protein cage and subsequently reduce different ions. The synthesized nanoparticles will be integrated with various specific receptors or probes such as peptide, antibodies, and aptamers as labels for developing biosensors and diagnostic imaging platforms. The sensing platforms can be developed for detecting pathogens or toxins from biological fluids or in vitro or in vivo imaging. This work will build synthesis capabilities and materials characterization approaches to address mission relevant issues to homeland security.

In FY 2008, we prepared Au-Ag alloys using native apoferritin as a model, consisting of a spherical protein shell surrounding an aqueous cavity of about 8 nm. Channels were generated by the multi-subunit construction of the apoferritin shell. Eight hydrophilic channels of approximately 4Å were thought to facilitate the passage of metal ions and small molecules of appropriate size into the protein cavity. Recent studies demonstrated that in the presence of urea, these apoferritin channels have sufficient flexibility to allow molecules larger than 4Å to penetrate the negatively charged apoferritin cavity.

During FY 2009, we successfully prepared Au-Ag and $Cd_{1-x}Zn_xS$ alloys using an apoferritin cavity. Simultaneously, we explored graphene, a new nanomaterial as a novel nanoscalfold, for biosensing and imaging. Details of this process are described below.

Tempalte Synthesis of Au-Ag Alloy. As continuous syntheses of Au-Ag alloys in apoferritin cavities occurred, we overcame the precipitation of Ag(I) ions in basic conditions. Two metal precursors, $AgNO_3$ and $HAuCl_4$, are pH and concentration sensitive. To avoid these issues, we first formed metal amine complexes, which are stable in basic conditions (pH = 8.0-10.0). The solution pHs were controlled by ammonia solution. Extra Au-Ag alloy particles could be easily separated because the filled apoferritins remain soluble. The core formation ratios, filled cores with respect to total apoferritin cores for all Au-Ag samples, were over 80 percent. Images showed the homogeneous particle size distributions to be with mean diameters of 5.60-6.20 nm, smaller than an apoferritin cavity (8.0 nm).

Biofunctionalization of Graphene with DNA/Adapmer. We choose DNA and aptamer as target biomolecules to study interactions between DNA/aptamer and functionalized graphene. Based on these findings, a novel graphene-DNA nanoscaffold will be developed for assays of genetic target and relevant biomarkers. This study demonstrated that single strand DNA can be effectively and promptly adsorbed onto functionalized graphene via hydrophobic and π-stacking interactions. In contrast, the double strand DNA presents much weaker interaction with graphene. Interestingly, the absorbed single strand DNA can be effectively protected from enzymatic cleavage, which is encouraging for potential graphene based biomedical applications involving complex cellular and biofluids samples. In addition, the absorbed DNA can be effectively desorbed from graphene surface via hybridizing with complementary DNA. Based on unique features of the interactions, a novel DNA-graphene fabricated optical nanobiosensor has been demonstrated for DNA assay with facile design, excellent sensitive improved selectivity, and biostability.

Graphene-Based Biosensors. We studied the direct electrochemistry of protein using glucose oxidase as a model molecule and demonstrated the direct electron transfer reaction of protein on the grapheme surface. Experimental data showed that graphene can provide an effective mircoenvironmental for protein to perform direct electron transfer reactions. Also, a novel glucose biosensor based on immobilization of glucose oxidase on graphene/platinum nanoparticles hybrid nanocomposite films fabricated on the surface of glassy carbon electrode was developed. Graphene has been explored as an alternative to electrocatalytic material for biosensor applications. This glucose biosensor modified with hybrid nanocomposite has been investigated, which has a good linear range (up to 2.5 mM, with a low detection limit of 0.6 μM), good reproducibility, and long-term stability. The interference from ascorbic and uric acids were negligible comparing with the response to glucose. The biosensor has been successively applied to detect glucose in human plasma sample with a good recovery.

During FY 2010, we will continue to pursue multiple metal alloy nanoparticles with optical and electrical properties and focus on the increase of nanoparticle crystallinity, which show strong luminescence and band gap properties to develop these nanoparticle based biosensing/bioimaging. We will also continue to study the graphene as nanoscalfod for biosensing/bioimaging.

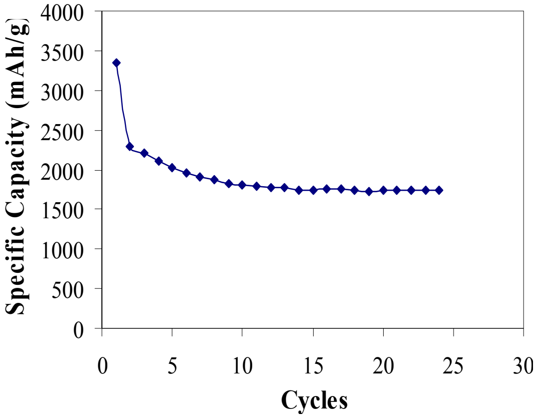
Development and Understanding of Nanostructured Materials for Advanced Energy Storage

Jason Zhang, Daiwon Choi, Donghai Wang, Jie Xiao, David Wang

◆ Fundamental improvements to electrochemical storage performance are essential for emerging applications, particularly in the transportation and electricity production sectors. ◆

Advanced batteries, in particular the high power/energy lithium ion, have been identified by DOE as critical enabling technologies for the development of advanced, fuel efficient vehicles, including plug in hybrid and electric. The applications are still limited by several barriers, including reliability, longevity, safety, and cost concerns. Higher energy and power than the current lithium ion are highly preferred and, as with the plug-in hybrid required for the applications. Given that the performance of electrochemical storage devices intimately depends on the properties of their electrode and electrolyte materials, the emerging applications require transformational materials that can demonstrate a much improved charge transport and electrode kinetics and a satisfied structural and interfacial stability as well as enable high voltage and multi- electrons per redox center for high energy density while being cost-effective.

One group of materials that potentially satisfies the stringent requirements are nanomaterials. However, there has been lack of fundamental knowledge about the roles of nanostructure materials in energy storage and scientific understanding on the processing of nanostructures, both concepts of which would help design and develop optimized nanostructures for electrochemical energy storage applications. Accordingly, our project focuses on: 1) a mechanistic understanding of the effects of nanostructures or architectures on electron/ion transport, electrode reactions, and charge storage at the nanoscale, and 2) the development of transformational electrochemically active materials via synthetic approaches that enable cost-effective, scale-up production of nanostructures with desirable features for energy storage applications.



Cycling behavior of nano porous silicon coated with carbon by a chemical vapor deposition method.

In FY 2008, our research focused on understanding the charge transport in nanostructured materials and the initial synthesis and assembly of anode, cathode, and electrolyte/cathode interface nanomaterials for lithium ion batteries. Low temperature approaches, including template assisted as well as mechanochemical, were investigated and developed to make novel nanostructures of rutile TiO_2 anodes, high voltage $LiMnPO_4$ cathodes, and nano thin film coatings of electrolyte on $LiMn_2O_4$ cathodes. Along with selective structural and chemical analyses via advanced diagnostic tools (including nuclear magnetic resonance and transmission electron microscopy), electrochemical studies were performed to understand fundamental charge transport in the electrochemically active materials and the effect of processing/nanostructure on charge transport and separation.

We also initiated the computer modeling effort to understand and predict the nanosize effects on electron/lithium ion transport in the synthesized nanostructures. Modeling efforts established a computational framework that can be fully extended and deployed in successive years. We performed simulations aimed at determining the mobilities of coupled electron and lithium ion transport in polymorphs of TiO_2 using primarily molecular dynamics simulations. As part of this effort, we performed density functional theory calculations with periodic boundary conditions to estimate the relative stabilities of different possible TiO_2 polymorphs as a function of added lithium ion content.

Additional progress was made during FY 2009. Silicon based anode has been investigated via several approaches. First, electrochemical properties of carbon coated nanoporous silicon powder were investigated. The micron size nanoporous silicon particles were coated with approximately 6 percent weight of carbon by a chemical vapor deposition process. The chemical vapor deposition coated silicon shows stable capacity of more than 1600 mAh/g. The morphology change of the original silicon and carbon coated silicon before and after electrochemical cycling has been investigated. In a separate effort, self assembling approach has been used to prepare silicon graphene superstructures. The silicon based anode prepared by this method also shows more than 1500 mAh/g capacity in the first 10 cycles. The third approach to prepare high capacity silicon based anode is the gas induced three dimensional (or solid-liquid-solid) growth of silicon nanowires.

Silicon based anodes prepared by these three approaches have demonstrated an initial capacity of exceeding 1000 mAh/g.

Anionic sulfate surfactants has been used to assist the stabilization of graphene in aqueous solutions and facilitate the self assembly of in situ grown nanocrystalline TiO_2, rutile and anatase, with graphene. These nanostructured TiO_2 graphene hybrid materials were used for investigation of lithium ion insertion properties. The hybrid materials showed significantly enhanced lithium ion insertion/extraction in TiO_2. The specific capacity was more than doubled at high charge rates, as compared with the pure TiO_2 phase. The improved capacity at high charge/discharge rate may be attributed to increased electrode conductivity in presence of a percolated graphene network embedded into the metal oxide electrodes.

High-voltage cathode $LiMnPO_4$ has been prepared by several approaches. Capacity of $LiMnPO_4$ not only depends on milling time but also ball size. The 2 g material milled with carbon using 2 cm balls for 4 hours. Sample shows a capacity of approximately 143 mAh/g when discharged to 2 V. In another effort, $LiMnPO_4$ is synthesized from $MnPO_4 \cdot H_2O$ precursor precipitated via a spontaneous reaction. These $MnPO_4 \cdot H_2O$ nano plates react quickly with the lithium source and form a pure phase of $LiMnPO_4$ that has good electrochemical properties. The samples exhibit a discharge capacity of 115mAh/g (C/20 rate at 2.5 to 4.4 V).

During FY 2010, we intend to 1) establish capabilities of large scale high purity silicon nanowires, engineering them and developing lithium ion cells to assist, 2) develop approaches capable of scale up production for improved electrochemical performance, 3) study the lithium insertion and charge transport processes, and 4) develop and investigate methods that potentially transform electrochemical performance.

Engineering of Metal-Organic Frameworks Imbedded with Metal Nanoparticles for Catalysis Applications

Praveen K. Thallapally

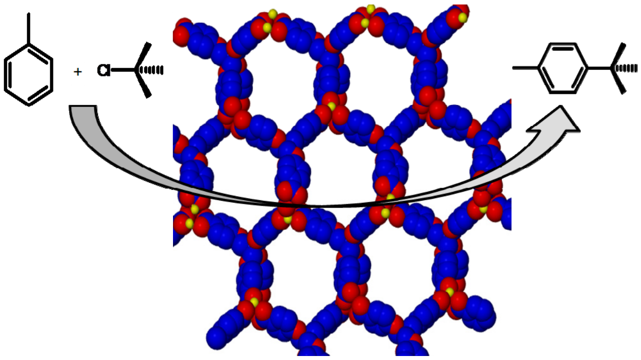
◆ Microporous coordination solids with acidic/basic sites and porous materials imbedded with metal nanoparticles will be explored for the catalytic conversion of CO, CO_2, and SO_x into useful chemicals. In addition, these materials can be employed to split water molecules into oxygen for fuel cell applications. ◆

For the past decade, microporous coordination solids have attracted considerable attention due to the high surface area and thermal stability. These materials have been explored for selective gas storage and separation applications. The ability to fine tune the pore size on a nanoscale while allowing the design of accessible metallic nanoclusters in a highly porous structure makes these compounds attractive for catalysis and sensor applications. Only a limited number of successful catalytic studies have been reported, and the chosen catalytic reactions were usually model reactions of little industrial interest.

Recent progress in organic and metal organic microporous materials synthesis has been important in developing robust sorbents for high capacity gas storage and separations. In theory, it should be possible to perform molecular catalysis in related materials. Metal organic frameworks are based on the coordination chemistry of metal ions or even tetrafunctional organic carboxylates linkers, leading to networks of perfect topologies, exhibiting molecularly defined cavities for adsorption of guest molecules, and imbedding of nanoclusters deep inside cavities. These networks will act as catalysts or, more generally, anchor functional species. Additionally, these networks are well organized and rigid, offering structural and thermal stability to generate void spaces for a range of applications in the solid state.

As the metal organic framework skeleton provides substantial pre-organization, this in combination with the many possibilities of selective functionalization made it possible to tune the molecule toward the desired application. We have made progress in designing and developing a superior catalyst based on metal organic framework that contains acidic/basic sites and synthesizing metal organic frameworks imbedded with various nanoparticles that act as a catalyst that contains a combination of alkali promoted base metals (Cu, Zn, Co, and Mo) immobilized on an organized network. Catalysts of particular interest included Cu–Co and Cu–Zn with promoters such as K and Cs. Once the specified catalyst is synthesized, the focus will be on the conversion of various gas mixtures to useful byproducts. Similarly, we are exploring other interesting challenges using the same catalyst for the splitting of water to oxygen for fuel cell applications.

Specifically, we performed a Friedel Crafts alkylation of toluene and biphenyl using tert-butylchloride in a batch reactor. The reaction was performed in a decane solution for 2 hrs at 170°C, with the resulting by products compared with acidic form of beta zeolite and aluminium chloride reported elsewhere. For toluene alkylation, two complexes showed high selectivity toward a paraoriented compound with greater than 99 percent conversion. For biphenyl alkylation using the same complexes, an outstanding selectivity was shown, with 100 percent conversion toward the paraoriented product, and ortho and disubstituted products were not observed during the reaction. However, the same alkylation reactions with another complex indicate a low conversion of toluene and biphenyl. The higher catalytic activity of the two complexes can be explained by the free metal sites found in those areas after removing free dimethylformamide and water molecules coordinating Zn_2 clusters.



Metal organic frameworks were synthesized using a single tetrahedral building block. Their catalytic properties toward alkylation of toluene and biphenyl showed high selectivity for a paraoriented product using these porous materials.

We will continue to develop a low cost catalyst based on microporous coordination solids imbedded with nanoparticles (Cu, ZnO, Ag, Au) for catalytic applications. We would like the opportunity to demonstrate selective conversion of CO_2/SO_x feed stream to useful chemicals and conversion of synthesis gas to methanol and higher alcohols. By immobilizing base metals on the organic framework surface, synthesized catalysts will have advantages over homogeneous catalysts in stability, size selectivity, recyclability, and high product yield. There is potential to produce new materials with significant, should the materials with promising properties in catalysis and sensor applications be discovered.

Friction Stir Welding of Creep-Resistant Oxide Dispersion Strengthened Alloys

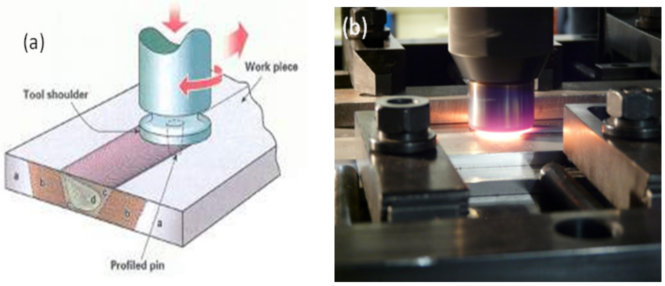
K. Scott Weil, Yuri Hovanski, Jens T. Darsell, Glenn J. Grant

◆ The simple act of joining materials ultimately places limits on their functionality in the intended application. For example, welded nuclear reactor material components are often rated for use at conditions far more conservative than those that would be employed if the welded region did not exist (i.e., material was monolithic). We are developing alternative methods of joining that overcome inherent limitations of the commonly employed fusion welding approach, particularly with corrosion lifetime. ◆

Because of their low cost, excellent thermal properties, and suitable corrosion and radiation resistances, ferritic/martensitic steels are primary candidates for advanced fast reactor cladding/duct materials, as well as fusion plant first wall and blanket structural materials. Unfortunately, the use of these alloys is limited to about 600°C due to a significant drop off in tensile and creep strength. It is well known that the incorporation of insoluble, nanoscale dispersoids in these materials greatly improves their high temperature mechanical properties. However, the preparation of such dispersion strengthen alloys is expensive and subsequent fabrication of componentry tends to be challenging, largely due to issues concerning joining. Liquid phase methods such as brazing and fusion welding lead to regions within joints that are devoid of dispersoids and associated strengthening effects, making fusion joined components susceptible to failure by creep. The objectives of this project are twofold: investigate an alternative solid state joining method (friction stir welding) for ferritic dispersion strengthen alloys, and identify strategies for reducing the cost of dispersion strengthening materials.

In friction stir welding, two metal work pieces are placed end to end, and a spinning tool is brought into contact along the common join line, simultaneously heating both pieces via mechanical friction. As the materials are heated, their flow stresses drop and the shearing action of the plunging tool causes plastic deformation to take place. As a result, material from each work piece flows into the other, leading to the formation of a solid state, metallurgical bond across the original join line. In dispersion strengthen alloys, our goal was to determine whether a sufficient concentration of dispersoids could be maintained across the weld region so that the joined part would exhibit creep strength essentially equivalent to that of the original pre joined material.

In FY 2009, we conducted a series of parametric welding studies on Kanthal APMT, a commercially available dispersion strengthened high chromium containing ferritic stainless steel. An envelope of successful welding conditions (such as linear speed, rotational tool speed, and rake angle) was identified and a set of 12 welded samples were fabricated for metallographic analysis. Based on our results, two promising welding conditions were chosen to prepare samples for high temperature mechanical testing.



(a) Schematic of friction stir welding, and (b) friction stir welding of ¼ inch thick dispersion strengthened steel plates at PNNL.

Microstructural analysis of the two sets of materials indicates that dispersoids are retained throughout the welds, consisting of three zones: core/nugget, thermomechanical, and heat affected. In all three, dispersoids appear to be distributed uniformly within the ferrite matrix. The average size particulate in the nugget (in friction stir welding, the region exposed to the highest internally generated temperature) is slightly larger (about 20 percent) than that observed in the other two zones or within baseline material outside the welded region. Additionally, we observed that machine operating conditions that generate higher temperatures lead to measurable growth of dispersoids, which can possibly degrade creep strength. Tensile and creep test specimens have been machined from the two sets of friction stir welding material and these are currently undergoing comparative testing at 600°C and 800°C along with baseline specimens prepared from unwelded Kanthal APMT. Our results have been or will be presented at two annual meetings (Fossil Energy Materials Conference and the Minerals, Metals, & Materials Society).

In FY 2010, we will complete the mechanical testing task initiated in FY 2009 and focus on aspects important to nuclear reactors materials welding: 1) characterization of corrosion properties of friction stir welding compared with fusion welded joints and baseline material, 2) developing methods of in situ quality control for thick steel friction stir welds (important in certification, inspection, and weld lifetime, to be conducted in collaboration with the South Dakota School of Mines & Technology), and 3) developing a friction stir based processing approach to synthesize oxide dispersion strengthened alloys directly for high temperature core and steam generator applications in collaboration the University of South Carolina.

In Situ Nuclear Magnetic Resonance Investigations of Trapping Mechanisms in CO_2 Storage

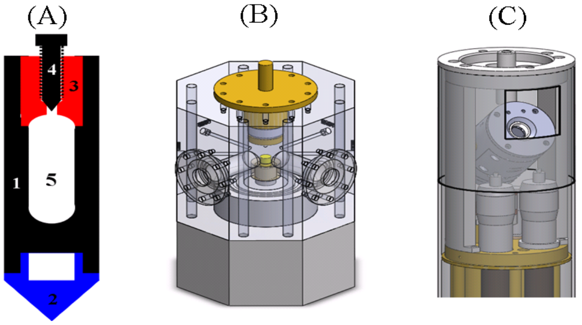
David W. Hoyt, Jianzhi Hu, Ja Hun Kwak, Jesse A. Sears, Kevin M. Rosso,
Andrew R. Felmy, Paul D. Ellis

◆ We propose to develop unique in situ nuclear magnetic resonance (NMR) capabilities, including the application of existing developed techniques, to advance the understanding of geochemical processes associated with the precipitation and dissolution of CO_2 at molecular level. ◆

Fossil fuel usage such as coal, a major source of CO_2 emissions to the atmosphere, will continue to provide a significant portion of total energy in both industrialized and developing countries. It is estimated that CO_2 global emissions to the atmosphere will double from 7.4 Giga tons of carbon (GtC) per year in 1997 to 26 GtC by 2100. Increased levels of greenhouse gases such as CO_2 are adversely affecting the global environment, as evidenced by recent trends in global warming and dramatic changes in weather patterns. These facts make it critical to develop technologies to stabilize CO_2 in the environment.

We propose to develop and apply unique high-pressure magnetic angle spinning (MAS) NMR capability for in situ characterization of mineral carbonation mechanisms and kinetics at super critical CO_2 pressure. Our studies will unravel the role of water activity for catalyzing mineral transformation to metal carbonates, understand water activity thresholds that enable mineral transformations, discover important chemical mechanisms involved in these transformations (dissolution, ligand-exchange, nucleation, etc.), and discover time-scales controlled by mineral transformation rates or by water availability.

In situ High Pressure MAS NMR Capability Development. This capability consists of a special high pressure sample cell (A), a high pressure sample loading chamber (B), and a special large sample volume (9.5 mm) MAS probe that provides low ^1H and low ^{13}C background (C). In order for NMR to work, the high pressure MAS NMR cell must be built with non-metals. Our unique design enables a combination of ceramics for holding the sample and plastics for high pressure sealing. A special NMR radio frequency transmitter and receiver coil is employed to achieve low ^1H and low ^{13}C background. Five high pressure MAS sample cells are being tested for withstanding and possible leakage at increased CO_2 pressure. The high pressure loading chamber has been pressure tested successfully to 2700 psi (180 atms). The construction of the MAS probe is being tuned for ^1H and ^{13}C at a magnetic field of 7.05 T. Special design is implemented so that a low ^{13}C and low ^1H background can be achieved.



The high pressure MAS NMR capability.

Ex situ ^{29}Si and ^{13}C NMR Investigations. Our focus is studying the metal carbonation of primary silicates using the mixture of Mg_2SiO_4+CO_2+H_2O at $scCO_2$ pressure with and without both CO_2 and H_2O. About 1.0 g samples of Mg_2SiO_4 and H_2O with a 1:1 weight ratio are loaded into a stainless steel bottle reactor. The CO_2 pressure inside the reactor is 80 atms. A single peak corresponding to bulk Mg_2SiO_4 is observed at -52 ppm. Only hydrolyzed products (i.e., H_2SiO_4) are observed at -74.4 and -81.5 ppm. The portion of hydrolyzed Mg_2SiO_4 as determined by the relative peak areas changes from 1.6 percent (20 hour reaction) to 1.9 percent (4 days) and to 3.2 percent (7 days). This result indicates that hydrolysis is fast at short reaction times but then slows. This is likely because the formed H_2SiO_4 hinders further hydrolysis. The ^{29}Si spectrum of Mg_2SiO_4+CO_2 at 80 atms has a reaction time of 20 hours, where only the peaks corresponding to Mg_2SiO_4 are observed. This result indicates that no reaction occurs if no H_2O is added. The peaks corresponding to the reaction products are about -91 ppm (should peak), -101.5 (main peak), and -108 ppm (shoulder peak) respectively. Based on these peak areas, about 7.9 percent of the Mg_2SiO_4 are reacted for 20 hours, while about 47 percent of Mg_2SiO_4 are reacted for 4 days continuous reaction. This ratio has increased to about 67 percent when the reaction time increased to 7 days.

Our preliminary results sufficiently demonstrate that ^{29}Si and ^{13}C MAS NMR are sensitive probes to investigate the detailed reaction mechanisms. The sensitivity at natural abundance should be sufficient for our proposed ex situ NMR studies. We will take advantage of using ^{13}C enriched CO_2 so that reaction dynamics with a time resolution as short as minutes can be probed. For FY 2010, we propose using our unique in situ high pressure MAS NMR probe so that reaction intermediates, products, absorption, and desorption mechanisms, including the dynamic behavior of the reaction, can be continuously monitored using a single sample. The results from our ex situ ^{29}Si, ^{13}C MAS NMR studies on Mg_2SiO_4+CO_2+H_2O systems are currently being summarized into a manuscript for publication.

Ion Beam-Nanoparticle Interactions for Radiation Detection

Marvin G. Warner, Yanwen Zhang, Jay W. Grate

◆ This project is designed to gain a fundamental understanding of the scintillation properties of semiconductor nanoparticles and to test the hypothesis that their radioluminescence properties correlate with the easily observed photoluminescence properties. Once complete, these studies will lead to a predictive understanding that enables a rational approach to the use of engineered nanomaterials in radiation detection applications. ◆

Recently, there has been an explosion of scientific interest in semiconductor materials in nanoparticle form, where quantum effects play a role in their optical and electronic properties. Called quantum dots, these semiconductor nanoparticles are typically made with a semiconductor core, a shell of additional inorganic material of a different composition, and an organic surface layer to stabilize the dot and prevent aggregation. While photoluminescence properties of quantum dots, which depend on parameters such as size, shape, and composition, are relatively well-understood in the open literature, research on the materials' radioluminescence response to ionizing radiation (e.g., ion beams, alpha and beta particles, and gamma rays) is just commencing. Studies have focused primarily on the empirical development of individual quantum dots containing composites to prove that they scintillate. Even more noteworthy is the lack of correlation between well-characterized photoluminescence properties and by extension their composition and structure, with the radioluminescence responses observed upon exposure to ionizing radiation.

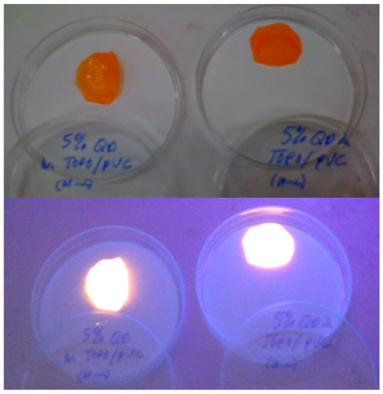


Image showing stabilizing polymer films containing luminescence quantum dots before (top) and during (bottom) irradiation with an ultraviolet light source.

If a correlation exists between photo and radioluminescence responses, then the first predictive understanding of the radiation physics of quantum dots will be developed. Knowing how photo properties correlate to radioluminescence responses would allow a synthesis of new material for radioluminescence applications a priori to possess specific characteristics. If there is no direct correlation, these studies will represent some of the first measurements of energetic ion interaction with quantum dots, determine the potential as materials for ionizing radiation detection, and provide insight into chemical composition and structure effects on radioluminescence properties. Moreover, systematic studies will help understand scintillation mechanisms, where photo-luminescence consists of photon excitation and emission processes and radioluminescence includes ionization energy deposition, electron hole production, migration and recombination, and photon emission and absorption properties and qualities.

Under this project, we will understand the correlation of photo and radioluminescence properties in nanostructured materials, including quantum dots characterization, synthesis, and physical measurements through integrated research. In FYs 2008 and 2009, we investigated how dot composition, shell structure, surface modification, and local environment influence photo and radioluminescence properties, measuring parameters such as fluorescence quantum (light) yield, ion induced luminescence spectra, resolution, and decay time. We investigated the synthesis of a wide range of quantum dots, including but not limited to CdSe, CdSe/ZnS, CdSSe, and CdSTe. These materials were produced using previously published methods adapted in our laboratory for these studies.

Once materials were synthesized and purified, stabilized polymer films were produced using methods developed in our laboratory for analysis using the ion beam system. The thin films were characterized using scanning electron microscopy to determine their morphology and quality such that the stabilizing organic ligand on the quantum dot surface served as film plasticizer. This served the dual role of stabilizing the dots against aggregation or decomposition while affording films that were pliable, rugged, and easy to handle from one measurement apparatus to another. Using the films, we measured ion and electron induced luminescence of the quantum dots as a function of loading (by weight %) into the polymer matrix and for the first time to correlate the observed radioluminescence properties successfully to measured photoluminescence properties of the same film.

In FY 2010, we will continue measuring radioluminscence response of specific quantum dots materials to correlate how changes in structure and functionality affect observable properties. Namely, we will focus on three parameters: quantum dot size, chemical functionality, and homogeneity of the resulting polymer films formed to stabilize the quantum for photo and radioluminscent measurement.

Leak Rate Measurements for Prototypic Pressurized Water Reactor Primary Water Stress Corrosion Cracks

Mychailo B. Toloczko, Stephen M. Bruemmer

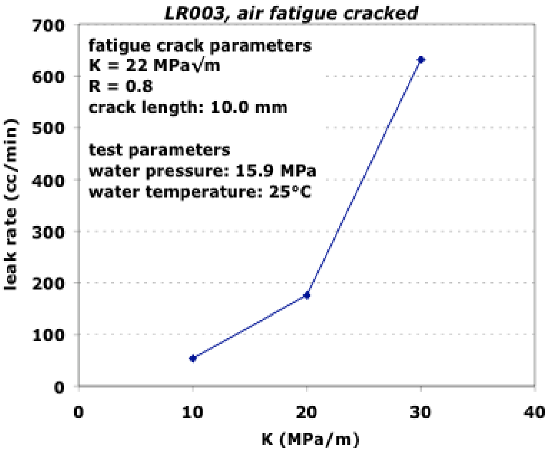
◆ Leak rate measurements of through wall stress corrosion cracks in light water nuclear reactor primary cooling pipe systems are needed to establish a sound leak before break criterion for stress corrosion cracks in these piping systems. The goal is to establish a laboratory-based experimental method to reliably measure leak rates in prototypic through wall stress corrosion cracks. ◆

Leak before break is a criterion to determine what safety measures are needed for light water nuclear reactor primary cooling pipes in the event that a crack forms and grows. Using a combination of experimental measurements, computer modeling, and statistical analysis, it is possible to predict with high accuracy whether a cracked pipe will leak before it catastrophically breaks. In the event that catastrophic failure is predicted to occur before a leak is detected, it is necessary for the utility companies to install massive pipe restraints and shielding at a great cost. DOE and several other governmental regulating bodies are strongly involved in the development and use of this criterion so that it is used accurately and correctly. Thus, there is strong interest both from the government and utility companies in determining whether piping systems will leak before breaking.

The leak before break analysis models, which were originally developed for fatigue cracks, are presently being modified to predict leak or break for stress corrosion cracks. An important part of this process is generating accurate assessments of leak rates in through wall stress corrosion cracks. Contemporary methods used for measuring leak rates in fatigue cracks are not suitable for measuring leak rates in stress corrosion cracks.

This project will develop a unique laboratory-based experimental method to measure reliably and relatively inexpensively leak rates in prototypic through wall stress corrosion cracks. The technique undergoing development makes use of state-of-the-art equipment and methods used to measure stress corrosion crack growth rates in materials for these piping systems. The existing equipment is being modified to allow growing a crack into a specimen and then measuring the leak rate through the crack when the crack has reached a pre-determined length. The experimental technique will be assessed on a fatigue crack and then on stress corrosion cracks grown into an alloy 182 weld metal sample and an ally 600 base metal sample.

In FY 2008, we modified the necessary laboratory equipment to allow leak rate measurements and preparing a fatigue cracked specimen to test the initial equipment modifications. For FY 2009, a suitable technique to modify a test specimen for leak rate measurements was developed, along with our completing baseline modifications to allow leak rate measurements using our state of the art crack growth test systems. Shakedown testing was then completed on three fatigue cracked specimens, with the tests providing valuable information on optimizing the leak rate equipment, properly preparing a specimen for leak rate testing, and on conducting a leak rate measurement test. Leak rate versus stress intensity (a measure of crack opening load) was obtained at room temperature on the third air fatigue cracked specimen as shown in the figure. Measured leak rates scale well as a function of crack exit opening with values in the literature for other leak rate measurement techniques showing that this method is viable.



Leak rate as a function of crack opening load for a fatigue cracked specimen tested at room temperature.

During FY 2010, leak rate measurements through specimens with prototypic stress corrosion cracks will be performed. Based on further consideration of the experimental data required to adapt leak before break models to stress corrosion cracks, two new tasks have been added to the project. The first task is to develop a technique to allow in situ measurement of the water pressure at specific locations inside the crack, and the second is to develop high resolution techniques to characterize crack opening and crack surface roughness after a leak rate test is complete. Adding these tasks establishes a capability to provide a complete set of experimental data needed to adapt the computer models. A technique to perform the pressure measurement has already been determined and will be tested in FY 2010. Methods for high resolution crack morphology measurement will also be investigated during FY 2010.

Material Interface Optimization in Extremely Thin Adsorber Photovoltaics

Tiffany C. Kaspar, Timothy C. Droubay

◆ To meet the world's growing demand for energy, breakthrough technologies such as nanostructured photovoltaic (solar) cells are required. This project investigates the fundamental charge transport properties of relevant photovoltaic materials to aid in material selection and optimization. ◆

Nanostructured solar cell designs utilizing novel materials are necessary to realize a revolution in solar cell efficiency and cost. One such design, the all-solid extremely thin absorber solar cell, consists of a nanostructured *n*-type semiconductor (ZnO) coated with a thin layer of photon absorber material (CdTe) and impregnated with a *p*-type semiconductor (CuSCN). Others have shown solar conversion efficiencies of 2.3 percent for the ZnO/CdTe/CuSCN structure, so there is room for significant improvement. To achieve highly efficient charge separation and transport in extremely thin absorber solar cells, the materials must be engineered such that the energy band alignments at the heterojunction interfaces are favorable for the desired charge transport (electrons into *n*-type ZnO and holes into *p*-type CuSCN). Despite the crucial importance of the resultant band alignments to the overall photovoltaic efficiency, heterojunction band alignments in solar cell materials are rarely measured directly. By directly measuring the band alignments with x-ray photoelectron spectroscopy, this fundamental study will open new paths to material selection, optimization, and solar cell design.

The thin film heterojunction chosen for the first band alignment measurements by x-ray photoelectron spectroscopy was insulating ZnO on the *n*-type transparent top electrode $(In,Sn)_2O_3$ (ITO) because these oxides are easy to work with and the heterojunction is utilized in many technological applications. Pulsed laser deposition was utilized to deposit 10 Å or 20 Å ZnO on ITO (1000Å)/quartz as well as thick ZnO and ITO reference standards. For 10 Å ZnO on ITO/quartz, the valence band offset was found to be -0.17 eV, making the conduction band offset -0.44 eV if the band gap of ITO is assumed to be 3.1 eV. This offset is favorable for electron transfer from ZnO to ITO.

However, for 20 Å ZnO on ITO/quartz, the band offsets were found to be unfavorable: valence = +0.41 eV and conduction = +0.14 eV. The thickness dependence of the band offsets indicates significant band bending at the ZnO/ITO interface. Band bending results in a 0.58 eV energy barrier for electron transfer into ITO, which makes electron transfer highly unfavorable. This is an unexpected result, as electron transfer between the two semiconducting oxides is generally assumed to be facile. Doping the ZnO *n*-type may improve the band alignment; work is underway to investigate the band offsets of *n*-type Al-doped ZnO/ITO.

Despite its wide application in solar cell devices, the electronic structure of the *p*-type inorganic semiconductor CuSCN has not been explored either theoretically or experimentally. Thus, basic information such as what causes *p*-type behavior and what the role defects play in the conductivity is lacking. To remedy this, we performed density functional theory electronic structure calculations of β-CuSCN (hexagonal crystal structure). Results for the band structure of CuSCN were somewhat unexpected. CuSCN was predicted to have an indirect bandgap, contrary to literature reports of a direct optical gap. Further, the bottom of the conduction band was found to consist of cyanide (C≡N) antibonding states, which gives CuSCN more of a "molecular" character than similar materials. It was found that Cu vacancies were necessary to generate *p*-type conductivity.

To corroborate the density functional theory calculations, CuSCN films were deposited and analyzed. Dropwise solution deposition onto a heated substrate (80°C) produced films, which were too rough for optical measurements but crystallized in the desired β phase. To generate an optically transparent, uniform film, spin casting (3000 rpm) of CuSCN dissolved in propyl sulfide was attempted. This method resulted in the desired transparent, well-adhered films which gave good optical absorption data, but remained amorphous after post-annealing. The bandgap calculated from the absorption data was in the range 3.85-3.88 eV, which is consistent with the (broad) range in the literature and an experimental effort that will be continued into FY 2010. Once crystalline films are successfully obtained, the theoretical and experimental results will be submitted for publication (manuscript already in progress).

In addition to continuing the work described above, measurements of ZnO deposited on CdTe will be initiated in FY 2010. Efficient charge transfer from CdTe to ZnO is crucial for photovoltaic performance, but the band alignments have not been investigated to date in the literature; this work will constitute the first reported results. Optimization of this heterostructure may provide a path to significant photovoltaic efficiency improvements. The CdTe/CuSCN heterojunction will also be explored, and the theoretical results described above will aid in guiding optimization schemes.

Measurement and Modeling of Slag Critical Viscosity, Optimization of Slag Chemistry, and Refractory Degradation in Coal Gasifiers

S. K. Sundaram, Siva P. Pilli, Kenneth I. Johnson, Rick E. Williford, Josef Matyas, John S. McCloy,
Jarrod V. Crum, Carmen P. Rodriguez, Alejandro Heredia-Langner, Peter C. Rieke

◆ Conversion of coal into clean burning liquid fuel shows significant promise from economic, environmental, and security perspectives. However, the full potential of gasification technologies for solid feedstocks has not yet been realized because of several factors, mainly cost and technical drivers. The primary objective of this project is to develop advanced models, materials, and sensors for the slagging coal gasifier to enable clean coal technologies. ◆

A slagging coal gasifier has extremely challenging environment inside: high temperature (1300 to 1600°C), large and sudden temperature variations and thermal stresses, alternating oxidizing and reducing conditions, high pressure, corrosive slag, and erosive residual particulates. The latest system clearly shows that the refractory performance is still a critical issue, and there is still a need to develop better refractory materials for this industry. The present project is an integrated approach to modeling, experimental validation, and sensors for slagging coal gasifiers.

On sensor development, millimeter waves of electromagnetic radiation in the 30 to 1000 GHz range are ideally suited for remote measurements in the harsh environments of gasifiers. PNNL is operating a state of the art dual channel millimeter wave passive radiometer/active interferometer. The heterodyne receiver system allows for radiometric measurements up to at least 1600°C in harsh environments. Interferometry arises through the mixed "video" from a 137 GHz narrowband local oscillator, allowing measurement of volume expansion/level change and viscosity.

Under this project, we measured the critical viscosity and used the data to develop a slag submodel to predict realistically the slag viscosity and flow as a function of slag chemistry and temperature. We have measured the slag refractory interaction parameters and developed a refractory degradation submodel to predict and verify the refractory corrosion/erosion and spalling. Such a model would be used to adjust the gasifier operating conditions (e.g., temperature) or slag properties to minimize the refractory corrosion while maximizing the coal throughput and conversion. In addition, the project also evaluated protection schemes for refractories. The overall goal of this research is to develop a model that will predict operating parameters (temperature, pressure, and corrosion limiting additives) that will best balance the conflicting requirements of high carbon conversion efficiency and increased refractory life.

Specifically, project progress during FY 2007 showed promise, as we made significant progress in modeling. The refractory degradation submodel was ready for expansion. The slag flow submodel was tested with our experimental data set. Two refractory spalling models were completed. With experimental validation efforts underway, we used statistical models to design a slag chemistry test matrix that will cover the U.S. coal slag chemistries. We prepared and characterized 20 test slags in our laboratory and measured the slag viscosities and critical viscosities of selected slags. In addition, extensive refractory slag interaction was completed. Experimentally measured slag penetration depth was fed into the refractory degradation model, and the experiment viscoelastic properties of select slags also were fed into the slag flow model. We integrated all existing glass/slag capabilities to adapt and use for this project. We also established and tested a new dedicated high temperature electrochemical testing setup for rapid screening of materials corrosion in melts.

In FY 2008, we applied a refractory degradation submodel to predict the failure region and modes using experimental slag penetration data. The submodel was modified to represent a hot wall gasifier and tested with our experimental dataset. A third refractory spalling model on a composite diffusion coefficient that connects physical processes and refractory chemistry was completed. We also studied the refractory slag interaction in reducing atmosphere study. Experimentally measured slag penetration depth and slag viscosity in reducing atmosphere were provided for validation of the refractory degradation model. We measured slag viscosities and critical viscosities of select slags in reducing atmosphere. The experiment viscoelastic properties of select slags were also fed into the slag flow model. Additionally, we developed chemical and electrochemical schemes to protect refractory.

Our FY 2009 the objective was to determine if STAR-CD could adequately model slag formation in a coal gasifier and predict slag spalling, penetration into the refractory wall, and reaction with the refractory. The major problem is that the current coal combustion model (and any modifications made to it) run only in the steady state mode and are not time dependent. However, film formation and flow problems such as a viscous slag layer on the wall can be modeled by STAR-CD, but apparently only in a time dependent mode. Thus, we have a basic disconnect between the two model parts.

Most of the empirical viscosity models of coal slags available in the literature are applicable to only limited ranges of temperature and composition. To develop a reliable slag viscosity model, additional data are needed. Slag viscosity was measured under air or reducing atmosphere (calculated $pO_2 \sim 1.2 \times 10^{-12}$ atm at 1400°C) at temperatures in the range of 1150 to 1550°C on 63 statistically designed slags, including 5 actual coal slag compositions and 4 validation slag compositions. The Arrhenius equation, with coefficients A as constant and B expressed as linear function of mass fractions of nine major components, was used to fit the viscosity/ temperature data. This Arrhenius relationship represented the relationship of tested slags reasonably well. The capability of the developed model to predict the viscosity of coal slags under reducing atmosphere was found to be a superior to a number of the most commonly used empirical models in the literature that are based on simplified oxide melts and British or Australian coal ash slags.

A refractory protection method was demonstrated in the laboratory scale. The method includes the steps of: 1) determining the effect of chemistry change on viscosity of the slag formed, 2) selecting the chemistry change that will lead to a sharp increase in slag viscosity, 3) designing a crystalline compound containing the chemistry that will increase the slag viscosity on its contact and reaction with the refractory, and 4) impregnating at least a portion of the refractory material with the crystalline compound(s). The crystalline compound at least partially fills a portion of the refractory material and serves to increase the viscosity of a slag material significantly when the slag contacts the compound, reducing the slag's ability to penetrate the refractory material and induce spalling of the refractory.

A millimeter wave heterodyne radiometer/ interferometer was used to study the infiltration of molten simulated coal slag (Wyoming Powder River Basin) into chromia-based refractory (Serv95) at 1450°C. Slag was melted in an alumina crucible at 1300°C, the pre heated refractory brick was placed in the molten slag, and the assembly was heated to 1450°C and monitored for several days. Observed phenomena included: slag melting and slumping, slag reboil/foam with oxygen evolution, and eventual failure of the alumina crucible through corrosion by the molten slag.

Overall, our 2009 project work yielded a poster and a paper being presented at the Pittsburgh Coal Conference 2009, and a paper was published in the conference proceedings.

Multicomponent Assembly to Achieve Charge Separation and Transport for Energy Conversion

Daniel L. DuBois, Xiao-Dong Zhou, Jun Liu

◆ This project will provide a fundamental scientific understanding of how to construct structured, functional, and organized nanoarrays capable of precisely delivering both protons and electrons to molecular catalysts for energy conversion. Our work will provide a better understanding of the multiple scales of architectures essential for solar fuel production and fuel cells. ◆

An abundant supply of clean and affordable energy is vital to the economic growth, quality of life, and security of the United States. The increasing energy demand will create worldwide competition for the gradually depleting fossil fuel reserves, endangering our quality of life that depends on a supply of energy at a low cost. On the other hand, increasing greenhouse emission is mostly likely linked to global warming. The concentration of carbon dioxide – the key contributor to global climate change in the atmosphere – is at the highest recorded level since records began and will increase further. The need to increase our energy supply while simultaneously reducing carbon dioxide emissions is one of the major challenges facing our global society today.

The specific aim of this project is to construct organized multiscale materials containing arrays of nanorods, nanotubes, or nanochannels that allow for efficient electron and proton transfer over nanometer dimensions. We wish to discover new approaches for multiscale assembly to achieve efficient energy conversion and improve our understanding of electron and ionic conductivity in such multicomponent systems. Our approach involves a shift in perspective in materials science from one of obtaining a single material with optimal properties to precisely assembled multicomponent materials composed of designed functional materials (for electron and proton transport and catalysis) integrated across a range of scales from the size of individual molecules through nanoscppic and microsopic scales to macrosopic devices. The demonstration of highly active integrated structures will provide an excellent basis for designing more complex multiscale structures such as membranes that integrate the functions of light-harvesting and charge separation, proton and electron transport, and catalysis.

In FY 2009, research on developing general strategies for immobilizing molecular catalysts on conducting surfaces continued, but the focus shifted from metal oxides to using glassy carbon electrodes to avoid poor conductivity and accessibility to conducting metal oxide electrodes. Research in each of the four areas described in the previous year was continued and a fifth approach, electropolymerization, was added.

- *Adsorption*. A new catalyst $[Ni(P^{Ph}_2N^{R'}_2)_2(NCMe)][BF_4]_2$ (where $R'=C_6H_4(CH_2)_5CH_3$) was synthesized with the objective of introducing a more hydrophilic substituent on the arene ring to promote adsorption onto hydrophobic electrode surfaces such as glassy carbon. This complex adsorbs onto glassy electrode surfaces, electrochemical activity appears to be preserved in this process, and catalytic activity for hydrogen production is also observed for the adsorbed species. This result indicates that further effort in this area is warranted and would contribute to the overall goal of achieving catalytically active electrode surfaces.
- *Catalysts Confined in Thin Layers of Ionic Liquids*. In FY 2008, the primary focus was on the use of [BuMeIm] [NTf_2] as an ionic liquid. Encouraging results were obtained in that catalyst **1** retained its electrochemical and catalytic activities when confined to the electrode surface using a thin film of this ionic liquid. To explore the potential of ionic liquids, we studied two new ionic liquids in FY 2009: $[C_{12}H_{25}P(C_6H_{13})_3][(CF_3SO_3)_2N]$ and an ionic liquid formed by the protonation of dibutylformamide with $H(CF_3SO_3)_2N$. Due to its highly hydrophobic character, thin films of $[C_{12}H_{25}P(C_6H_{13})_3]$ $[(CF_3SO_3)_2N]$ are more stable than those of the previously studied ([BuMeIm][NTf_2] ionic liquid). However, incorporation into these films resulted in low activity attributed to the inability of the liquid to provide an adequate supply of protons (i.e., the acids used were of low solubility in this ionic liquid). The catalytic performance is enhanced by incorporation of Nafion (a known proton conductor), but performance was still less than desirable. To overcome this problem, the ionic liquid formed by the protonation of dibutylformamide with $H(CF_3SO_3)_2N$ was studied as a thin film containing catalyst **2**. An active catalyst was observed with a turnover number of at least 50,000 and frequency of approximately 10 s^{-1} over a period of 1.5 h. This performance is quite exciting, and studies in this area will be pursued in FY 2010.
- *Catalysts Immobilized in Nafion Films*. In this area, mixtures of ionic liquids and Nafion were used to improve the stability of the ionic liquid films to dissolution and the ability complexes **1** and **2** to undergo electrochemical reduction compared to these complexes in pure Nafion films. These goals were achieved, but the performance of these films is still not comparable to those of the pure ionic liquids or to catalysts immobilized by adsorption.

- *Covalent Attachment of Catalysts to Metal Oxide Surfaces*. Studies of ferrocene derivatives using the same linkers as described for the Ni complex **1** in FY 2008 were used. In this case, redox active ferrocene waves were observed. These results support our conclusions from studies in FY 2008, where we concluded that covalent attachment of catalyst **1** was occurring but the failure to observe electron transfer to this catalyst was due to restricted motion of the catalyst due to multisite attachment. Further approaches to covalent attachment are not planned at this time.

- *Electropolymerization*. Extensive studies of a new complex **3** prepared for electropolymerization onto glassy carbon electrodes were carried out in FY 2009, and an invited paper has been published on this work. Complex **3** is an active electrocatalyst for hydrogen production in acetonitrile solutions with a turnover rate of 56 s-1 and an overpotential of a new cyclic 1,5-diaza-3,7-diphospha-cyclooctane ligand was prepared with phenyl substituents on phosphorus and (thiophene-3-yl)phenyl substituents on nitrogen. This ligand reacts with $[Ni(CH_3CN)_6][BF_4]_2$ to form the corresponding $[Ni(P^{Ph}{}_2N^{Ar}{}_2)_2(NCMe)][BF_4]_2$ complex **3**, an active electrocatalyst for H_2 production. Kinetic studies indicate that the catalytic rate is first order in catalyst and second order in acid at low concentrations of acid. At higher concentrations, the catalytic rate becomes independent of acid concentration. The rate-determining step at high acid concentrations is attributed to the elimination of hydrogen from a reduced nickel species. The modest overpotential of 280 mV and a turnover frequency of 56 s^{-1} confirm that **3** is a relatively active catalyst for H_2 production in acetonitrile solutions. Oxidation of the pendant thiophene substituents of **3** results in the formation of films on glassy carbon electrode surfaces. However, these films are not electroactive, and electrocatalysis of proton reduction is not observed with these modified electrodes. This approach will not be pursued further.

Over the past two years, five different methods of immobilizing molecular electrocatalysts for hydrogen production have been studied. Of these five, direct adsorption of the molecular catalysts and use of thin films of ionic liquids containing dissolved molecular catalysts have shown the most promise. It is these approaches that will be used in FY 2010 to expand to catalytic electrodes for carbon dioxide reduction and for modifying electrodes composed of arrays of nanorods or nanotubes.

Multiscale Charge and Ion Transport Simulations for Nanostructured Electrodes

Kevin M. Rosso

◆ This project will develop and perform first ever simulations of collective charge transport dynamics from the atomic to micron scales for coupled charge and ion transport in polycrystalline metal oxide electrodes. We will also develop a deep fundamental understanding of the basis for charge and ion conductivity in select systems. ◆

Titania is an attractive alternative for carbon-based anode materials in lithium ion batteries due to its high surface area, chemical stability, and high theoretical capacity. Several polymorphs of titania have been shown to benefit significantly from nanostructuring or from the incorporation of nanoporosity. Increased rate capability, capacity, and tolerance for strain due to lithium insertion/extraction have all been reported for titania nanomaterials. Although nanostructuring and nanoporosity offer improved performance due to higher contact areas between electrolyte-electrode and shorter diffusion distances for lithium ions and electrons, there is a lack of fundamental understanding of the effects on charge and ion transport efficiency of nanosizing electrolyte-electrode interfaces and of the interdependence of electrode materials and electrolytes, contact areas, and diffusion distances, thus preventing reliable predictions of performance.

A long-term goal of our research is the discovery of design principles for nanostructured metal oxide electrodes that maximize charge and ion diffusivity. The first step is to improve our understanding of charge and ion transport in electrode materials such as the titania polymorphs. In particular, two fundamental questions are how charge carrier diffusivity is correlated to ion diffusivity at the level of individual electrons and ions, and how this coupling affects the overall transport efficiency and conductivity.

Our FY 2009 activities focused on performing molecular dynamics simulations of the kinetics of coupled electron and lithium ion transport in Li_xTiO_2 polymorphs for comparisons with experiments and also to examine fundamental processes that potentially impact anode performance in lithium batteries. We concentrated on the two most stable and most studied titania polymorphs: rutile and anatase. Lithium insertion in both polymorphs to form Li_xTiO_2 compounds has been studied extensively over the last few decades. Additionally, lithium insertion in macro and micro sized rutile crystals has been shown consistently to be limited at room temperature with published lithium mole fractions of $x = 0.0008$, $x = 0.02$, $x = 0.03$, $x = 0.07$, and $x = 0.15$. Higher mole fractions can be reached at higher temperatures.

Molecular dynamics simulations were performed with a potential shell model to investigate the diffusion of lithium ions and electron polarons in rutile and anatase. Simulations of an isolated lithium ion in rutile predicted fast diffusion in the c-axis channels with an activation energy of 0.05 eV, which corresponds to a jump rate of 4×10^{11} s^{-1} and a diffusion coefficient of 9×10^{-5} cm^2s^{-1} at room temperature. In anatase, the activation energies for intra and inter octahedron lithium hopping were computed to be 0.02 and 0.39 eV, respectively, and the lithium diffusion coefficient was four to five orders-of-magnitude slower than in rutile.

In the presence of an electron polaron, lithium hopping was predicted to be affected up to four hops away. The effects were more pronounced in rutile, where the first energy minimum along the c-axis was absent from strong lithium-electron electrostatic interactions along open c-axis channels. Combining lithium and electron polaron hopping and electron transfer rates, a coupled diffusion mechanism emerged, where electron polarons diffuse hop rapidly back and forth around lithium ions. This process can lead to the occurrence of an instantaneous driving force for lithium hopping. The lithium ion electron polaron binding energies were found to be large, with a stronger binding in rutile than in anatase: 0.45 and 0.28 eV, respectively, suggesting that at low lithium mole fractions, lithium ions and electron polarons form strongly correlated pairs.

In FY 2009, computational molecular simulation with a key staff member of coupled lithium ion/electron transport kinetics results led to the publication of two manuscripts and submission of two others in high quality journals. For FY 2010, we will build on these simulations to include new approaches that allow us to reach further upward in scale toward the transport behavior within whole nanocrystalline titania grains, across grain boundaries, and ultimately between model networks of grains. The new simulations will include Poisson-Nernst-Planck diffusivity modeling combined with classical density functional theory, kinetic Monte Carlo simulations of grain scale coupled diffusivity, and embedded cluster calculations of diffusivity across grain boundaries. Also, we will continue to collaborate closely with the nuclear magnetic resonance project team to compare predicted lithium ion hop rates directly with measurements. Generally, our efforts will help address a critical bottleneck at the national level that crosscuts several next generation energy based technologies. Our ultimate goal is to provide a basis for data interpretation and decision making for materials design.

Nano and Micro-Engineered Solid Adsorbent for Rapid CO_2 Capture and Regeneration

Wei Liu

◆ Success of this project will lead to CO_2 capture technologies with 70 percent potential cost-reduction to the conventional amine scrubbing process for capture of CO_2 from combustion flue gases. This represents billions of dollars per year in cost savings for U.S. industries if CO_2 capture and sequestration regulation is implemented. ◆

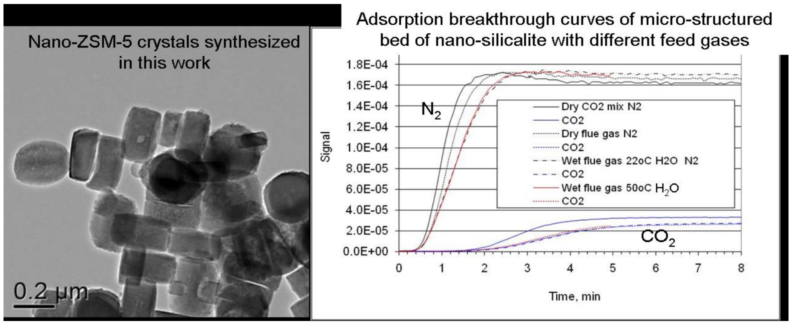
Various technical approaches to CO_2 capture in literature have covered most separation technology areas, including solvent absorption and adsorption, membrane, and distillation. Based on energy costs and process efficiency, adsorption is the most attractive for CO_2 capture from low pressure, diluted flue gas streams, although certain technical liabilities must be overcome. Among conventional exotic adsorbent materials, zeolites have been selected for overall consideration of feasibility, innovation opportunity, durability, manufacturability, and ultimate cost.

This project applies nano- and micro-materials design and engineering approaches toward innovation of adsorption separation process technologies. Inorganic zeolite materials are chosen because of their proven molecular sieving functions, chemical and thermal stability, and the ability of large-scale manufacturing. Our technical approaches include developing cost-effective process ideas for synthesis of nano-sized zeolites that enhance the intrinsic adsorption/desorption kinetics rate dramatically and address a critical challenge in implementation of adsorption technologies; creating an innovative, specific framework or surface substitution of the zeolite lattice structure to reduce the heat of adsorption and selectivity of CO_2 adsorption under flue gas conditions; and developing micro-structured adsorbent beds of unique performance features such as low ΔP and fast mass and heat transfer to enable rapid adsorption/regeneration cycle and maintain long-term durability in large-scale operation. The original ideas are critical to development of a low cost, practical adsorption process.

In FY 2008, we evaluated approximately 34 solid adsorbent samples for CO_2 and water sorption on a thermogravimetric analysis. Because water vapor is ubiquitously present in CO_2 gas mixture, resistance of a solid adsorbent to moisture sorption is critical for a practically viable adsorption process. We modified a flow adsorption/regeneration testing apparatus, with reversible, selective CO_2 adsorption confirmed. Structured adsorption beds were prepared with ceramic honeycomb and porous stainless steel sheet support structures. Different types of adsorption/regeneration kinetics enhancement over the commercial adsorbent bead was demonstrated in the flow system, representing a breakthrough in adsorption bed technology.

During FY 2009, we have been successfully synthesizing nano-sized ZSM-5 crystals of different Si/Al ratio by inventing a self-assembly multiphase flow reactor, which is first in this zeolite synthesis field. The resulting crystal is pure and has uniform particle size distribution. The synthesis time is within a few hours, much shorter than one week growth time typically used in the conventional autoclave process. The process is very promising to be scaled up as a low cost, nano-zeolite manufacturing process. We also demonstrated nano-silicalite as a feasible adsorbent material for CO_2 capture under realistic flue gas conditions in a continuous flow adsorption bed. The adsorbent showed rapid adsorption/regeneration kinetics (regeneration in about 2 minutes) and excellent stability with a wet simulated flue gas consisting of N_2, CO_2, O_2, H_2O, SO_2, and NO. No performance decline was observed during repeated adsorption/regeneration cycles.

Additionally, we compared different adsorbent beds with the same zeolite adsorbent material (commercial 13x), extruded beads, crushed particles, micro-structured bed. The micro-structured bed of present innovation provides faster adsorption/regeneration kinetics and better adsorbent utilization than the conventional packed bead bed at approximately 1 to 2 orders-of-magnitude lower pressure drop. One journal article was published, and one presentation was given to a professional conference.



Nano-zeolite crystal and adsorption curves.

In 2010, we will focus on enhancing the CO_2 adsorption capacity with the novel nano-zeolite and scale-up of both the material synthesis and micro structured bed for extensive adsorption/regeneration tests with simulated flue gas mixtures.

Nanoscale Tantalum Oxide Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells

Jin Yong Kim, Yongsoon Shin

◆ Currently, there is a strong need for a reduction or replacement strategy for platinum-based catalysts in the DOE fuel cell program, which aims to reduce stack costs by 2015 to 25 percent of the current level. We will develop economical catalysts for polymer electrolyte membrane fuel cells in order to replace the current expensive platinum based catalysts. ◆

Cited in seminal reports by the National Academy of Sciences, American Physical Society, and DOE, one of two bottlenecks to the success of polymer electrolyte membrane fuel cells is cost and developing an appropriate means of hydrogen storage. Recent economic studies indicate that fuel cell stack cost can be reduced by decreasing or eliminating the amount of platinum required in the cell electrodes, the largest quantity of which is employed in the cathode where it catalyzes the oxygen reduction reaction. While substantial progress has been made in understanding why platinum is such an effective catalyst for oxygen reduction reaction and in explaining the catalyst degradation mechanisms that currently limit the operational lifetimes of polymer electrolyte membrane fuel cells, little success has been achieved in identifying promising alternative electrocatalysts.

We aim to investigate the synthesis, microstructure, and properties of a new polymer electrolyte membrane fuel cell catalyst. We recently studied carbon supported nanoscale tantalum oxide materials that show promise as an alternative oxygen reduction reaction electrocatalyst in partial or full replacement of platinum. This project will focus on synthesizing an optimized form of this material via a sol gel approach. Methods will be employed to investigate the microstructure and composition of the catalyst and catalyst support, particularly along the interface where the two materials meet, and catalytic activity will be measured using a previously established half-cell measurement in an effort to coxygen reduction reactionelate interfacial structure and composition to catalytic activity.

In FY 2008, we developed economical oxygen reduction catalysts for polymer electrolyte membrane fuel cells by replacing expensive platinum with tantalum oxide. The basic concept was to enhance catalytic performance by making nanoscale tantalum oxide/carbon composites that contain increased triple phase boundaries working as reaction sites for oxygen reduction. The novel direct synthesis technique was developed to produce nanoscale tantalum oxide/carbon composites. When these composite catalysts were tested using a conventional static three electrode half cell, the maximum mass specific reduction current at 0.7 V vs. normal hydrogen electrode (NHE) was obtained from the composite containing 30 wt percent tantalum oxide. The mass specific reduction current of his sample was approximately 9 percent compared to platinum.

In FY 2009, we set up a rotating disc electrode for electrochemical analysis and kinetic study, optimized the tantalum oxide content and particle size for maximum performance, and identified effects of dopant such as tungsten and titanium on electrochemical performance. The amount of tantalum oxide was lowered, and best performance was achieved with 17 wt percent of tantalum oxide. The study shows well-dispersed nanoscale tantalum oxide (less than 10 nm) on a carbon support. A rotating disc electrode test was conducted using 1 N sulfuric acid as electrolyte and gold as a counter electrode. The voltage sweep was performed between 1.1-0.2 V with respect to the NHE at 5 mV/sec. Results revealed slight lower oxygen reduction potential (nearly 0.95 V vs. NHE) than platinum (1.01 V). In terms of mass specific current density, the tantalum oxide/carbon composite catalyst with 17 wt percent tantalum oxide exhibited 2.6-5 percent at 0.6 V (vs. NHE) and 27-30 percent of maximum current density at 0.2 V. The relative performance of tantalum oxide was higher at low rotating speed due to diffusion limitation compared with platinum, and lower at high rotating speed.

Adding tungsten improved the electrochemical performance of tantalum oxide/carbon composite catalysts. Optimal performance was achieved with 32 mol percent replacement of tungsten with tantalum. For this tungsten-doped tantalum oxide composite catalyst, the maximum current density at 0.2 V was nearly 50 percent of platinum. At 2400 rpm where diffusion limitation is minimized, the composite catalyst revealed 7.2 percent at 0.6 V and 35 percent at 0.2 V. The area specific current density with almost 0.2 mg/cm^2 loading of active materials was up to 16 percent at 0.6 V. Since these materials did not show diffusion limitation, the area specific current density was improved up to 4.5 times when active material was loaded 5 times. With maximum loading, the current density reached up to 66 percent compared with platinum. These results demonstrate the potential of nanoscale composites as an economical alternative for platinum catalysts.

In FY 2010, we will investigate and optimize doping transition metal elements such as tungsten and titanium, study long term stability of tantalum oxide based composite catalysts and the effects of the valence state of transition metals and its role on electrochemical performance, and explore intermediate size full cell tests using the best composite catalyst.

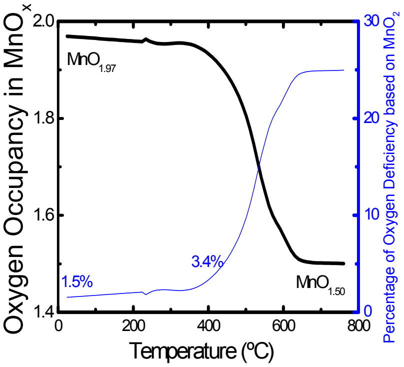
Simultaneous Charge Transport in Laterally Confined One-Dimensional Systems

Xiao-Dong Zhou

◆ We will investigate the transport of electrons and ions in hydrothermally grown nanometer wires of lithium ion and lithium iron phosphate. Success in this project will produce fundamental insights into charge transport phenomena in laterally confined systems. ◆

Simultaneous electron and ion conduction is of great importance in understanding transport phenomena and for developing various energy conversion and storage systems. Of particular interest is charge transport on the nanometer scale, within which confinement effects may be observed. Electron and ion transport lie at the heart of recent DOE sponsored workshops that addressed the current status and possible future directions of some important research areas: solar energy utilization, solid state lighting, hydrogen fuel, superconductivity, and energy storage.

In this project, crystal and local chemical structures will be evaluated, and transport dynamics will be investigated by in situ nuclear magnetic resonance and impedance spectroscopy with a blocking electrode. The structure transport property relationship will be evaluated with respect to short- and long-range ordering of lithium ions, channel size for ion migration, exchange between lithium and transition metal ions, and magnetic ordering. A transport theory will be developed based on a space charge model and will be closely coupled with experimental studies.



Oxygen occupancy of $MnO_{2-\delta}$ nanowires as a function of temperatures, measured in air.

In a conductor with reduced dimensionality, electron motion is free electronlike along one-dimensional system axes, such as quantum wires or in planes parallel to the surface in a two- dimensional electron gas structure. One can assume that electron transport is parallel to confining potentials; hence, homogeneous transport properties in reduced dimensionality systems can be discussed in the same context as bulk systems. Further, homogeneous transport properties enable macroscopic phenomenological parameters such as mobility, conductivity, and thermopower to be measured in appropriately designed experiments.

During FY 2008, we employed in situ nuclear magnetic resonance with respect to ZnO proton characteristics to investigate proton dynamics in ZnO nanorods. Protons were clearly present in ZnO at ambient temperature; however, protons remained at elevated temperatures (between 200 and 500°C) only in some highly aligned and uniform nanowires. The transport dynamics of protons associated with defects in ZnO nanorod lattices were determined from measurements of the temperature dependent spin lattice relaxation time. Because we could differentiate signals associated with proton defect states from the weakly bound surface hydroxyl groups, site specific dynamic information was obtained.

For FY 2009, $MnO_{2-\delta}$ nanowires were chosen for our studies because they exhibit rich chemistry and crystalline phases. Also, the use and modeling of nanometer-scale MnO_2 in the fields of catalysis, supercapacitors, and battery electrodes prompted further exploration to understand anomalous observations of size dependent behavior. In most of these applications, the redox reaction between Mn^{4+} and Mn^{3+} contributes to the unique property of MnO_2. Therefore, it was necessary to study nonstoichiometric chemistry and its role on electronic conduction.

The MnO_2 nanowires were synthesized by oxidation of $MnSO_4$ with ammonium persulfate in a hydrothermal reactor, and precipitates were filtered and washed for further characterization. The nonstoichiometry of nanowires was studied by using a combined differential scanning calorimetry and thermogravimetric analysis. Electrical conductivity and electrochemical performance of MnO_2 nanowires as battery electrodes will be reported. MnO_2 is known with various allotropic polymorphs, which differ in distribution of Mn ions in octahedral sites of the oxygen framework. X-ray and electron diffraction indicated that the as synthesized MnO_2 phase is αMnO_2. With calculated oxygen occupancy in MnO_2 nanowires, oxygen vacancies are consistent with a previous study that shows a reduction of Néel temperature in MnO_2 nanowires due to changes of oxidation states of Mn ions. Alteration of oxidation states in MnO_2 would result in a variation of charge carrier density. Indeed, electrical measurements showed that MnO_2 nanowires were conducting.

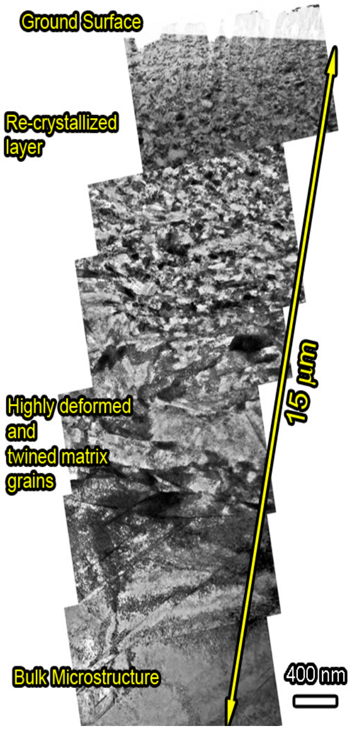
The activation energy for the electronic conduction of microparticles is about 0.095 eV compared with 0.22 eV for nanowires. The greater activation energy in MnO_2 nanowires is attributed to the enthalpy for oxygen vacancy formation. Defect chemistry modeling showed that the enthalpy for oxygen vacancy formation was about 0.38 eV in nanowires. MnO_2 nanowires were tested as the potential cathode for rechargeable lithium ion batteries and showed good cyclability.

Surface Damage and Environment-Induced Cracking Precursors in Light Water Reactor Components

Matthew J. Olszta, Danny J. Edwards, Bruce W. Arey, Stephen M. Bruemmer

◆ Unique insights into the influence of surface preparation and reactor aging will be obtained defining relevant precursor states for the first time. The fundamental understanding of near surface microstructures as a function of key service parameters will lead to improved predictive methodologies for crack initiation and significant advances in the non destructive detection of crack precursors. ◆

The results of this project will enable a better understanding of surface structure and morphology in light water reactor components exposed to practical surface treatments and service environments. State-of-the-art, multiscale investigations of the restructured surface will provide quantitative insights into the depth, extent, and microcharacteristics of near surface damage layers. Detailed knowledge of deformation microstructures will improve understanding of time dependent corrosion/oxidation processes and stress corrosion crack initiation pathways. Exposure to light water reactor environments at high temperatures will help elucidate the development of precursor states in restructured near surface morphologies leading to crack initiation and propagation. Using site specific sample preparation techniques allowed by focused ion beam milling, the entire surface and near surface regions can be prepared and analyzed as one continuous uniformly electron transparent sample. The preparation and analysis will allow for a complete picture of surface structures and precursor crack initiation sites in light water reactor components.



Brighfield transmission electron microscope montage of a 304 SS surface polished with 60 SiC grit at 100 N of force and displays a recrystallization layer. The entire damage gradient from the surface to the bulk can be observed in this figure.

During FY 2009, two primary goals were accomplished. The first was to develop a transmission electron microscopy sample preparation technique that would provide a uniform electron transparent model at least 15 to 20 µm into the sample. This was accomplished using a unique focused ion beam technique that provided a view of the entire surface damage gradient such that we could explore the microstructure from the surface into the bulk. The second goal was to recreate surface damage conditions observed in industrial components using controlled laboratory experiments. Using a Struers polisher/grinder, we were able to first reach a level of polishing that induced little to no damage on the surface but also removed any contamination from the cutting process used to make sample coupons. This was considered to be a satisfactory starting condition for all future grinding experiments. We were then able to use the heaviest grinding settings to recreate surface damage microstructures that resembled those observed from in service sample components.

Our observations have shown that regardless of surface grinding conditions, there is a recrystallization layer composed of elongated nanocrystalline grains at the surface layer. The evolution of the damage microstructures into the sample was similar as well in each level of grinding, but it was determined that larger grinding forces corresponded to deeper damage into the bulk. The key point is the recrystallized layer and what it means to crack initiation precursors. Using transmission electron microscopy, we have fully characterized this layer and are beginning the long-term exposure of these layers to light water reactor water conditions under constant stress states.

In FY 2010, we plan to continue exposure of these damaged surface layers in light water reactor water conditions. At various time increments, samples will be removed to examine the evolution of crack initiation precursors through the surface damage layers. Comparing the starting microstructures to the oxidized/corroded surfaces will provide possible insight as to how stress corrosion cracking commences in these materials and whether we can provide early detection systems from the results.

Mathematics and Computing Sciences

A Data Virtualization Architecture

Eric G. Stephan, Karen L. Schuchardt, Ian Gorton

◆ To protect vast amounts of raw scientific data, we are providing high-performance software services for provenance and metadata tracking, storage mechanisms, and a virtualized search engine to find results with ease. ◆

Today's large-scale science involves management of a petascale data stream obtained directly from experiments, theoretical computations, and simulations derived by further, often complex analyses. The data reside in different storage systems (i.e., spreadsheets, flat files, relational databases, high performance file systems) using different physical and logical models and incorporating varying degrees of annotation and provenance tracking. Addressing key scientific and national security challenges increasingly requires that multiple sources be accessed to solve a particular problem, more information be known about data history and derivation, and data be readily exchanged between various analysis programs that are often constructed as processing pipelines.

This project will define an architecture that uses semantic technologies capable of scaling to the needs of large-scale, data driven research. We propose a data virtualization architecture that defines core services for high performance provenance tracking and searching, a consistent and simple programming model for accessing data in a variety of physical stores, mechanisms to integrate raw scientific data files and provide virtualized query access, and an architecture upon which to experiment with advanced semantic query mechanisms. This work will result in components, services, and application programming interfaces (APIs) that create a data access and integration platform, enabling research teams to use system science approaches to address critical scientific challenges.

Research during FY 2007 focused in three areas: developing a provenance model for workflow capture based on the needs of Middleware for Data Intensive Computing (MeDICi), 2) defining and deploying a preliminary scalable provenance store architecture, and 3) demonstrating our capabilities by participating in provenance community challenges. We also worked to evaluate our approach and test its viability in the user community. The key to giving scientists the highest degree of confidence and helping to explain what happened and what resulted, provenance is a unifying mechanism to describe, annotate, and track relationships between data and to search for data in disparate data sources while retaining autonomy between data sources.

In FY 2008, we developed and deployed the Describe Anything API (DAApi) to provide a powerful recording interface that supports automatic graph relationship management flexible enough to apply to a variety of execution models. The DAApi interface defines core capabilities of the API, including basic storage. The WorkflowDAApi extension handles session management, and storage calls can be made for a number of resource objects. Actual storage was delegated to alternative implementations of the ProvenanceProvider, the second component of the interface. The third and optional part of the interface was ContentProvider, which enabled capture of physical files to the content store or an archive.

In FY 2009, we designed and prototyped a capability that leverages resource description framework named graphs to create and manage views as a server side function, simplifying user presentation of provenance data. Provenance capture as applied to execution oriented and interactive workflows is designed to record minute detail needed to support a "modify and restart" paradigm and re execution of past workflows. In our experience, provenance also plays an important role in human centered verification, results tracking, and knowledge sharing. To overcome the low-level of detail received from most provenance capture mechanisms, we needed it in a user oriented view. Our peer reviewed paper was presented to an Institute of Electrical and Electronics Engineers Practice and Theory of Provenance workshop. As the Defuddle parser continued to grow in usage, the Duke Comprehensive Cancer Center contacted our team to explore use of the Cancer Biomedical Informatics Grid. We also met with the National Center for Supercomputing Applications at the University of Illinois, where Defuddle is being used to describe binary data for the National Archive.

To demonstrate use of provenance in data intensive problem spaces, we applied provenance tracking within a MeDICi workflow to show the value of provenance in climate and atmospheric research, as sensor measurement models are generated from raw sensor data streams. For the demonstration, we leveraged the DAApi developed the previous year to collect provenance. To describe the provenance formally, we leveraged the International Provenance and Annotation Workshop Open Provenance Model that we helped co author. Because the captured provenance was such an extreme scale, a traditional large graph representation proved impractical. Instead, we developed a multi tier model that organizes the provenance so that it can be distributed and analyzed in smaller discrete chunks. Sample provenance can be compared side by side across a span of time to detect trends or anomalies with greater ease, lending itself to comparative analysis and visualization techniques such as qualified tree views.

A Modeling Approach to Understanding and Mitigating the Environmental Impacts of Tidal Power

Andrea E. Copping, Zhaoqing Yang, Rochelle G. Labiosa, Tayeun Kim, Thomas J. Carlson

◆ Energy from tidal currents has the potential to provide substantial quantities of clean renewable electricity; but significant uncertainties over environmental impacts remain. Predicting environmental impacts through integrative modeling will help decision-makers evaluate ecological risk and provide siting and environmental mitigation guidance to tidal power developers. ◆

Energy from ocean tides, waves, and currents have the potential to provide substantial quantities of clean, renewable energy. Numerous designs for ocean power turbines are becoming available. Regulatory agencies, including the Federal Energy Regulatory Commission (near shore, 3-mile limit) and the Minerals Management Service (outer continental shelf) as well as coastal states are developing regulations for leasing ocean space, licensing power plants, and assessing direct impacts of single devices on living marine resources. There has, however, been no systematic assessment of the impacts of ocean power farms on coastal waters.

Puget Sound has excellent tidal currents in close proximity to large urban centers, making it one of the top locations in the nation for tidal power. Permitting and regulatory processes are emerging for tidal power siting, but environmental uncertainty is a hurdle to development. To date, there are few tidal power installations worldwide, and little is known about direct or system-wide ecological impacts of tidal power devices. The objective of this project is to develop and calibrate a model that will enable high-resolution, accurate simulations of the system-wide hydrodynamic and water quality impacts of tidal power generation in Puget Sound. Predicting potential environmental impacts before devices are installed will inform siting, environmental assessments, and monitoring plans.

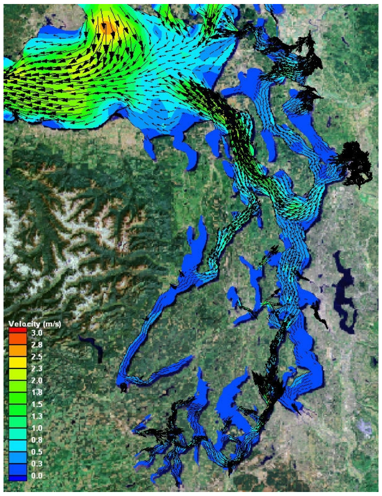
We developed a three-dimensional hydrodynamic transport model for Puget Sound using state-of-the-art Finite Volume Coastal Ocean Model (FVCOM) software developed by the University of Massachusetts that covers Puget Sound, the Strait of Juan de Fuca, and the San Juan Islands. Initial applications simulated Puget Sound hydrodynamics to evaluate ecosystem restoration projects (FY 2007) and examine potential impacts from weapons of mass destruction (FY 2008).

In FY 2009, we adapted the model to answer tidal power questions. Specifically, we expanded the domain across the U.S.-Canada border to include Fraser River, Georgia Strait, and continental shelf along the Washington coast and Vancouver Island. We added new functionality and selected a water quality model for Puget Sound to couple with the newly expanded hydrodynamic model. In addition to the modeling effort, we assessed acoustic imaging processing technology with an emphasis on visualizing interactions between marine species and tidal turbines.

Expanded Puget Sound Hydrodynamic Model. We coupled the expanded model with meteorological data and calibrated/validated the model against water surface elevation, currents, temperature, and salinity. In addition, we developed a forecast system that provides real-time information about the Puget Sound hydrodynamic and water quality conditions during tidal power simulations.

Coupled Water Quality Model. We coupled the expanded hydrodynamic model FVCOM to the estuarine ecosystem (water quality) model CE-QUAL-ICM throughout the domain and tested the resulting code. Currently, we are calibrating the coupled model for coarse resolution water quality simulations for the entire Puget Sound area and working to reduce run time so that the model will be capable of decadal simulations. Understanding system-wide water quality effects from tidal power development will help regulators and stakeholders assess ecological effects during initial stages in the site evaluation and permitting process.

Acoustic Imaging. We completed a preliminary feasibility analysis into algorithms to detect and extract features of interest (fish and marine mammals) for long-term studies. We determined that technological barriers could be overcome and that acoustic imaging could play an important role in tidal power monitoring studies.



Model-predicted Puget Sound surface water currents will inform tidal power siting and be used to assess system effects of tidal power installations.

A Statistical Framework for Integrated Explosives Detection

Kristin H. Jarman, Kenneth D. Jarman, Nathaniel Beagley, Mark F. Tardiff

◆ Next-generation devices for explosives detection and characterization need to be portable, robust, and insensitive to various backgrounds introduced by diverse environments. The current project facilitates this goal by developing integrated data analysis of information from different screening and detection devices. ◆

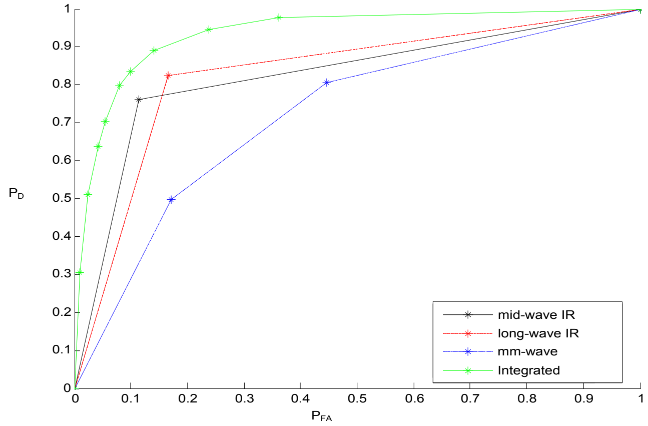
A number of advanced technologies are in progress for preconcentration and standoff and trace level explosives detection. Developed to work alone or in combination with other sensors, these technologies collect, pre-concentrate, and detect explosives and analyze those results in a manner that enable end users can make reliable decisions. To secure optimal performance, a decision analysis framework is needed to take data from multiple disparate sensors and convert the data into meaningful results. The objective of this research is to develop a sensor integration and decision analysis methodology for explosives detection that can propagate uncertainty through a multi-sensor detection system and perform Bayesian integrated explosives detection. A prototype for the framework will be developed and tested on data from publicly and privately available sources.

Two major tasks were performed in FY 2009. First, the two stage framework developed in FY 2008 was modified to include passive (standoff) detection in a crowded environment. Available data will be employed to demonstrate the effectiveness of the Bayesian framework in decision support. Second, a mathematical uncertainty propagation model was developed for the two different scenarios in combination with a simulation study to characterize performance and evaluate the effectiveness of the integrated approach to explosives detection.

The Bayesian framework has been applied to two operational scenarios: passenger screening and passive surveillance of people entering a large event. The first scenario was demonstrated on existing data in FY 2008. For FY 2009, available data were used to demonstrate the potential for the Bayesian framework in the second scenario. The specific case study used was passive screening of spectators entering a large venue using three different camera technologies: near-infrared, mid-infrared, and mm-wave. By implementing a Bayes net for large-event spectator screening, several insights were obtained. As we integrated the three data sources, we found that error rates were generally lower than if a single data source or two of the data sources had been used (refer to the figure). Layers of clothing on screened spectators affected performance of infrared cameras but not the mm-wave camera. From this combination, it was possible to mitigate the effect, making error rates higher than for infrared cameras alone. The nuisance parameter layers of clothing lowered overall performance of the integrated system because of reduced reliability of infrared cameras. This underscores the need for designers of such systems to understand how interferents, nuisances, and background clutter might adversely affect performance of individual sensors and integrated systems for explosives detection.

For the second task, a mathematical study answered several fundamental questions regarding integration of sensor data. Several key results were obtained. Particularly in a system with identical sensors, adding a new sensor always reduces error rate. However, the incremental improvement in error rate decreases as the number of sensors increases. This suggests a point of diminishing returns when adding new sensors to an integrated system. All other things being equal, a single stage system has lower error rates than a two stage (primary and secondary) system. Of course, due to practical considerations, a single stage system is not always feasible. Optimal configuration for any integrated system depends not only on individual sensor error rates but also on the effects of potential interferents or nuisances.

Two assumptions limit the framework to operational scenarios where such measurements are available. First, the framework developed in FYs 2008-2009 assumes that all sensor measurements are taken at the same time, with the exception of the primary vs. secondary sensors in the two stage airport screening scenario. It also assumes sensors are co-located, measuring the same thing at the same time. In response, we will investigate methods in FY 2010 for extending the Bayesian framework to applications where measurements are spread over time and/or space.



Results illustrating receiver operating characteristic curve of explosives detection system made of individual sensors and three sensors for large event spectator screening. P_D refers to probability of detection, and P_{FA} refers to probability for false alarm.

Adaptive Composite Analysis for Complex Systems

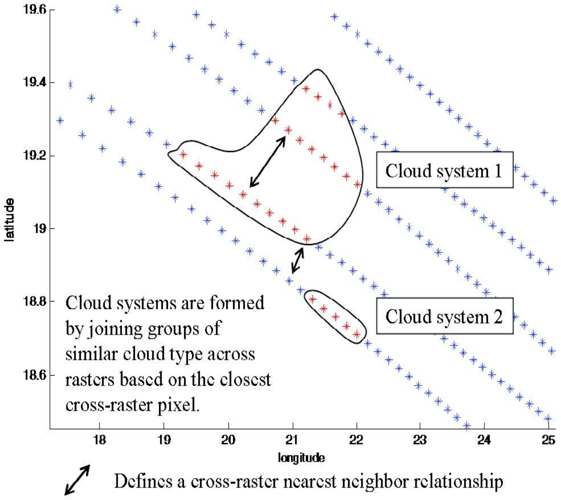
Amanda M. White, Christian Posse, Nathaniel Beagley, Paul D. Whitney, Stephen C. Tratz

◆ This research is aimed at enhancing the way disparate data source in a streaming environment can be fused to provide a more effective, complete description and retrieval of information, enabling scientists to manage information more efficiently. The benefits of this research are demonstrated in the context of anomaly detection in computer networks, object identification, and property correlation in satellite geophysical data. ◆

In recent years, advances in hardware technology have facilitated the ability to collect massive amounts of data continuously. This ability has led to several computational challenges: 1) algorithms are allowed only one pass over data streams, 2) algorithms must cope with temporal evolution of streams and can no longer hold all data in memory, 3) many data stream applications run in distributed environments and need to be fused, 4) visualization and interactive mining of massive data streams must be redefined entirely, 5) the tradeoff between accuracy and efficiency has become critical, and 6) real-time accuracy evaluation and formalization are required. Attempts at organizing and comparing fusing techniques for streaming data have been made only very recently. These efforts highlight the need for a framework within which rational fusion strategies for streaming data are developed.

The objectives of this project were to develop foundations of such a framework and demonstrate its benefits with two challenges: build efficient, adaptive, robust methodologies for detecting aberrant behavior in massive data streams for possible network monitoring use, and fuse data from multiple satellites to identify multi-measurement geophysical objects and measure statistical relationships between object properties. In FY 2007, we developed a comprehensive, five-level taxonomy (classification) that characterizes not only inputs and outputs of a fusion system but also relevant fusion processes and algorithms. This taxonomy forms the backbone of fusion framework. We also developed a novel methodology for adaptive and robust anomaly detection based on the Holt-Winters forecasting algorithm which, in its static and non-robust version, is used extensively in network monitoring solutions. During FY 2008, we developed an alternative anomaly detection methodology for real-time analysis of massive data streams based on a least squares estimation routine over time windows of multiple scales.

Fusion occurs at the degree of anomaly level to account for individual uncertainties in evaluating the uncertainty associated with the fused anomaly. We used the fusion framework to fuse anomalies efficiently across multiple streams into a single fused anomaly. Our fusion methods were applied to a large data set of cyber security network traffic data in which we successfully re-identified known malicious events and discovered new, previously undetected malicious events. The fusion detection work has been issued in a peer reviewed publication, and was presented at two conferences.



Example of cloud system identification from individual points.

We applied the data fusion techniques to satellite data to develop routines for identifying cloud objects efficiently in atmospheric data and for fusing data from multiple satellites and instruments to investigate correlations between co-located object properties. The purpose is to determine the statistical relationships between atmospheric phenomena measured by different satellites. This information may ultimately be used to improve climate models and their predictions. A canonical correlations algorithm was used to assess interactions between data sets. The canonical correlations algorithm was used because the problem requires treating the variables in a symmetric manner (i.e., not inferring cause and effect between them). In the taxonomy of fusion strategies, the satellite fusion work falls under symmetric feature fusion.

The final focus of this work was to integrate the satellite data fusion algorithms with the Middleware for Data Intensive Computing platform for complex and data intensive analytics. This integration allows distributing processing load among multiple computers and modularizing algorithmic steps so that improvements can be made to a part without affecting other modules of the process.

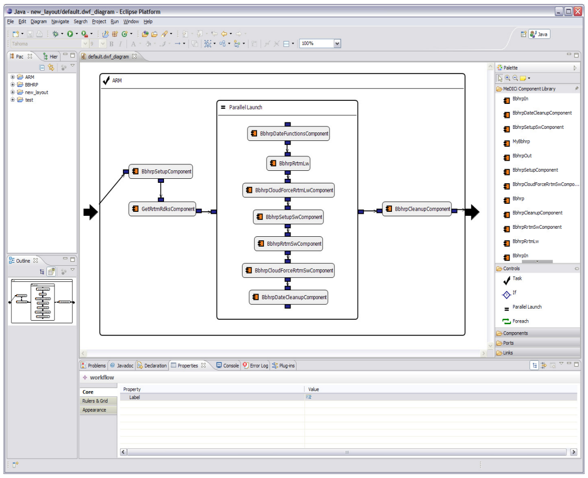
Adaptive Workflow in Data Intensive Environments

Alan R. Chappell, Ian Gorton

◆ This project produces a workflow design and management capability enabling researchers and analysts to exploit massive data sets and specialized compute facilities. This workflow system supports creation of complex analytic applications through the visual definition and execution of adaptive computational workflow pipelines. ◆

Domains from bioinformatics to intelligence analysis are experiencing an explosion in the availability and complexity of data. Diverse, complex data from the Internet, communication sources, sensors, and data-rich experiments produce unique problems in analysis and knowledge extraction. The high volume of data and the complexity of analyses demand longer duration processing capabilities that inundate current computation and communication infrastructures. Knowledge extraction, access, and storage of massive data require a change in data analysis that will facilitate human understanding and support well-informed responses and decision processes.

The complexity of domain analysis can be addressed through different computational systems and components. Workflow description and management have been used to enable more flexible composition of these components. Generally, workflow is defined as the order and restrictions in which steps in a process are performed. Beyond descriptions, workflow management systems maintain the automatic execution of a described workflow. By supporting workflow in data-intensive environments, researchers, analysts, and decision makers can make more effective use of massive data sets, high-performance and special-purpose computing facilities, and collaborative inputs from complex systems.



A screenshot from the workflow system interface showing user interaction to create computational pipelines with parallel execution.

Initially, our approach used an open standard Business Process Execution Language (BPEL) and supporting workflow management technologies for component orchestration in conjunction with the MeDICi Integration Framework (MIF) to provide underlying computational architecture. A prototype implementation of this system demonstrated that the design emphasized the strengths of both technologies and enabled a flexible, powerful computational environment. With this foundation, work in FY 2008 focused on design and development approaches for a user interface and interaction system. A goal was to develop a system that supported nonspecialists in workflow creation. Based on interactions with prototypical users, we created a series of visual designs that mapped proposed interactions using the workflow system.

Traditional approaches to creating this complex system would be expensive and produce a large code base. The model-driven architecture (MDA) software approach was chosen to address software complexity through the systematic use of information models and mappings to create robust, maintainable interactive systems automatically. Using emerging MDA environments and tools, implementation of the workflow interface enabled a user to work with visual artifacts at a familiar level of detail to draw a computation pipeline. With MDA capabilities, the system automatically updated a workflow model based on this interaction. When ready, the system transformed the model into a BPEL workflow model for deployment to a BPEL execution engine.

Research in FY 2009 broadened workflow interface capabilities by expanding boundaries beyond current MDA capabilities. One primary focus was supporting parallel execution of components using a natural, easy to visually define mechanism. This enables new communities of users to exploit available advanced computing environments like clusters. Combined with this effort was research to make effective use of the model-to-model transformation within MDA to simplify the process of creating the base interface and resultant BPEL models, thus enhancing system-wide robustness.

Another focus in FY 2009 was on adaptive workflow. With new control elements, users can visually describe desired adaptivity within the workflow, and the system would produce the appropriate BPEL implementing that adaptivity. The system was further enhanced with features defined in the original interface design, including the depiction of component libraries. Mechanisms to deploy workflows to a BPEL execution environment linked to MIF were also created. Together, these critical features enable users without extensive programming knowledge to understand and use the workflow system to accomplish complex tasks in data-intensive environments. This work was reported in one book chapter, four refereed conference papers, and one article in a refereed journal.

Biosignature Integration for Inference of Biomarkers from Complex Systems

Bobbie-Jo M. Webb-Robertson, Jason E. McDermott

◆ This research supports building and operating major forefront scientific user facilities by developing integration strategies for disparate data sources that compare biological and chemical information ranging from individual biomolecules to ecosystems. A generic data integration framework to support systems biology and diagnostic tasks would facilitate major scientific discoveries that would drive U.S. competitiveness. ◆

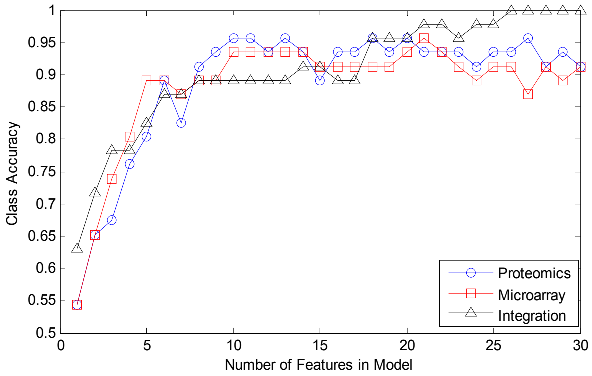
With the end goal of inferring system level biological activity, data integration is one of the challenges of modern biology. Though biology is often a data rich discipline, integration can fall short because of complex data types that do not have one to one mappings (e.g., proteins to genes). Specifically, the molecular footprint of many modern techniques such as mass spectrometry based proteomics is not linked to the biology in a direct path. These data contain hidden patterns that may be as complicated as shifts in entire populations or as simple as a set of spectrum peaks. Integrating the data from multiple technologies into an interpretable form to identify either a diagnostic pattern or underlying biological response requires developing and using powerful statistical approaches to manage the differences in resolution from the instruments.

The majority of research on biological data integration has focused either on extremely targeted problems, such as protein-protein interactions or diagnostics (e.g., cancerous or not). For a more generic approach to integration applicable to a wide-range of problems, we developed a Bayesian statistical framework that offers a visual interface to derive probability models and view classification results. Building the framework required merging the statistical methods into an easy to use and interpretable form for experimentalists. In FY 2007, we identified and modified an existing collaborative experimental data management system, defined the probability models to be used for several data sources from disparate technologies, and performed biological data mining for several systems under consideration (*Francisella novidica*, mouse). In FY 2008, we applied the integration approach for two biological problems on vastly different scales: pathogen exposure in a mouse model and uranium exposure in a periphyton community. We also developed a visualization for communicating the results to scientists performing the experiments.

During FY 2009, we released the first version of the software Visual Integration for Bayesian Evaluation (VIBE) and applied the methodology in vastly different problem spaces. In addition, we developed Stepwise Probability Based Investigation for Feature Selection (SPIFFS), a new algorithm to generate biosignatures of uranium exposure in a periphyton community.

VIBE. VIBE 2.0 was released as a standalone software tool that allows a user to explore effects of including or excluding specific data sources in a Bayesian fusion analysis. VIBE works by integrating probability models from multiple data streams. The software can either ingest pre computed probability models or create them from the raw data. The statistical methods used to derive the probability models and the data included in the fusion can be modified on the fly to analyze the system dynamically.

SPIFFS. The feature selection algorithm selects the set of features that most accurately classify “treatment” groups in a probabilistic manner from one or more treatment groups. The algorithm was used on data collected from an experiment on a periphyton community exposed to uranium at four doses, unamended and at 10, 100, and 500 µg/L, over the course of five days. Following collection of the periphyton the biomass was extracted and sent for mass spectrometry based proteomic and a tree-of-life microarray analyses, which yielded large amounts of data in over 10,000 and 12,000 potential markers, respectively. Statistical analyses reduced the candidate list of biomarkers to under 100 for each method and further feature selection using SPIFFS demonstrated that a biosignature derived from a combination of markers from the two data sets could separate the four exposure groups with more accuracy than either dataset individually, achieving 100 percent accuracy via cross validation at 26 features.



The number of features in biosignature versus classification accuracy derived from a partial least squares discriminant analysis on individual and integrated datasets demonstrates improved discrimination with a complex biosignature of proteomic and microarray markers.

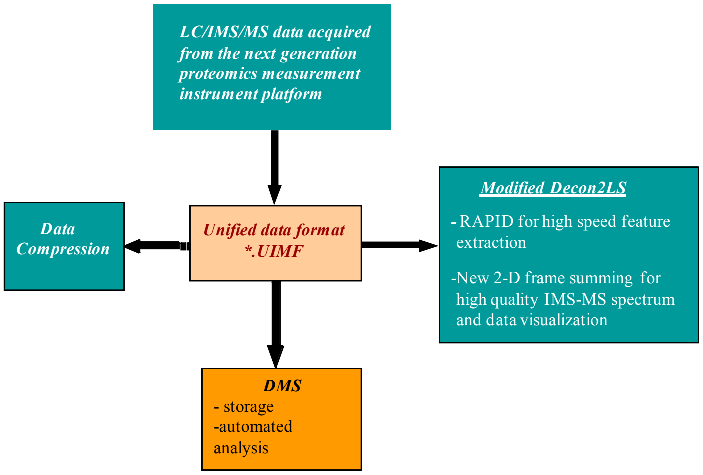
Computational Capabilities for Storage, Management, and Utilization of Large Data Volumes

Keqi Tang, Erin M. Baker, Nathaniel Beagley, William F. Danielson III,
Anoop M. Mayampurath, Richard D. Smith

◆ The next generation proteomics measurement instrument platform, which incorporates a liquid chromatography (LC) high efficiency electrospray ionization (ESI) source, ultra high-speed gas phase ion mobility separation (IMS), and high-speed time-of-flight mass spectrometer (TOF MS), is capable of generating data at extremely high speed (about 100 Mbytes/s) due to its unique high throughput sample analysis capability. This project focuses on developing and implementing new computational capabilities for effectively managing the massive volumes of proteomics data from the new instrument. ◆

The major proteomics challenge is to identify and quantify the full complement of proteins in generally small samples. Current proteomics measurement technologies involving the combination of a condensed phase (liquid or solid) separation and high performance MS can achieve very high resolving power (peak capacity of over 500 for single stage separation methods and approximately 3000 for multi-dimension separation methods). The limitation of these technologies is their low sample throughput, mainly due to the low speed of separation in the condensed phase. This project focuses on developing new computational capabilities for real-time data processing and display. The new software tools are developed to handle the extremely high data generation rate effectively by the next generation proteomics measurement platform. The developed data handling capability also includes efficient data compression, storage, and management necessary for subsequent data analysis.

To improve the proteomics measurement throughput, PNNL and other research institutes developed new instrumentation that combined IMS with MS. Using PNNL's ion funnel and multiplexed IMS technologies, sensitivity of the IMS/MS instrument was improved significantly. The key feature of IMS is the extremely fast speed of analyses: separation typically takes less than 0.1 s, much faster than LC separations (up to hrs). Combined with MS, IMS/MS can offer a comparable separation power with a 10- to 100-fold increase in throughput. The challenge is to handle the massive volume of data effectively from the instrument. For example, a single LC/ESI/IMS/TOF MS analysis may have 1000 to 10,000 discrete measurements steps in the LC dimension, each with 1000 steps in the IMS dimension, all of which are captured as separate spectra with intensity readings in 100,000 TOF bins each. This corresponds to approximately 10 terabytes of raw data per day from a single instrument, for which it is impossible to use the current methodology for data management.



LC/ESI/IMS/MS data management, processing, and visualization workflow.

In FY 2008, high performance data management capabilities for the new proteomics measurement platform were developed and tested for initial proteomic applications. New software tools needed to support the data volumes generated from the IMS/MS system and the ability to move and access this information were developed, including signal thresholding, data compression, and data conversion to a unified data format. The initial test showed that the data management workflow was capable of work effectively in managing data from the new instrument. The raw data files were further compressed to retain only essential information sufficient for subsequent informatics analysis before they were stored in the data management system.

New software tools for efficient data compression and storage capabilities were further integrated during FY 2009, with the current computational architecture to handle the high data generation rate (approximately 100 Mbytes/s) effectively through the new instrument platform. Specifically, Decon2LS, an algorithm for data processing and visualization, was modified to handle the large IMS/MS data set. A RAPID algorithm was incorporated into Decon2LS to gain the speed of IMS/MS feature extraction by 40 times compared with the original Thrash algorithm. The new two dimensional IMS/MS frame summing algorithm has also been developed to improve the spectrum quality and data visualization. All the new algorithms were tested using proteomics data from *Shewanella* and *E. coli* samples.

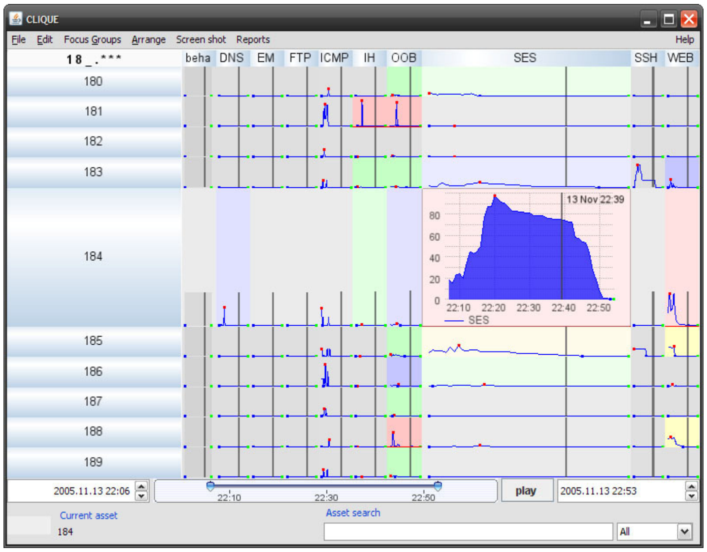
Correlation Layers for Information Query and Exploration (CLIQUE)

William A. Pike, Shawn J. Bohn, Joseph R. Bruce, Daniel M. Best

◆ Across domains, the need to analyze high volume streaming data visually is central to creating human understanding of patterns and trends. The CLIQUE project is developing analysis techniques that can help detect features embedded in these streaming data sets, such as anomalies in computer network traffic. ◆

The objective of the CLIQUE project is to develop new visual analysis methods that help humans discover and detect potentially malicious events in vast amounts of streaming data. The project has developed a set of software components that implement new algorithms for pattern discovery and new visual metaphors for displaying those patterns. Previous research in this area has focused on two standard approaches for event identification in transactional data: signature based methods and statistical anomaly detection. Signature based approaches are successful at identifying instances of known patterns, while anomaly approaches use general heuristics and statistical variances to identify patterns of interest. In practice, neither method alone is sufficient. Recognizing that a gap exists between signature and anomaly approaches, we have implemented a set of machine learning algorithms for use in either a supervised or unsupervised mode.

Because visual analysis of raw network transactions does not scale well to large data volumes, our method classifies data according to common attributes. Each class represents a category of behavior inherent in computer network data. In FY 2009, we implemented a classifier based on the QROCK algorithm designed for categorical data of the sort characteristic of network transactions as part of a pipeline built in PNNL's middleware for data intensive computing (MeDICi). This pipeline distributes data from a source of network flows through a classifier and aggregator to a set of visualization clients that have registered to listen to the data stream.



The CLIQUE interface summarizes large volumes of network data in real time using a matrix view that shows categories of traffic (in columns) and a network actor such as organizational unit (in rows). The interface uses a "rubber sheet" technique that allows the user to stretch it open to see more detail in a given cell.

We used heat maps to summarize trends in the streaming data. Heat maps are matrices in which cells are color coded to numeric values, allowing users to identify anomalous and correlated regions visually. However, heat maps have not been scalable beyond a few hundred dimensions in either rows or columns. Our approach to building heat maps for massive data sets is to reduce the data through multilevel classification. As heat maps are typically static, we have implemented a dynamic heat map display capability that allows analysts to track the high level behavioral patterns in streaming data. The heat map interface is interactive, allowing analysts to "play" live data and stretch open cells to see data charted in more detail. This interaction technique allows users to drill deeply into data while preserving its context. The coupling of the streaming classifier, MeDICi pipeline, and real-time visualization in a dynamic heat map is the primary technical contribution of this research. The impact to the end user is the ability to visualize high volume data in a much more condensed, information rich fashion than was previously available.

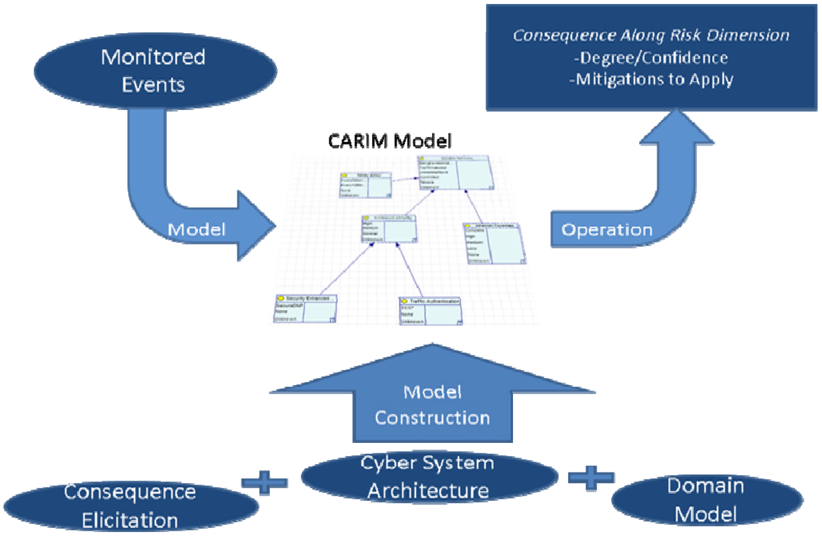
Our research has also explored how we could identify sequences of activity indicative of cyber threats. During FY 2008, we explored supervised learning to organize these groups into patterns that make sense to domain experts. We initially implemented and extended the Very Fast Machine Learning toolkit for mining high volume data sets. We also engaged domain experts to explain their data usage and analytic expectations that resulted in a set of scenarios that detail the requirements for network monitoring and forensic applications. This initial classifier and work with experts enabled our implementation and demonstration in FY 2009 of a functional prototype for real time monitoring of larger volumes of cyber data than has been previously possible. Portions of this work are being incorporated into tool suites deployed to government customers, and we are extending the tools to accommodate data from other domains.

Cyber-Attack Risk Inference Model

Stephen D. Unwin, Patrick R. Paulson, Jonathan Young

◆ This project uses formal risk modeling methodologies to describe cyber assets of an installation in terms of the risk that compromise of those assets will present to the organization. We feel that this approach will improve the ability of administrators of cyber systems to prioritize their time and resources, offering improved security for both cyber systems and associated infrastructure. ◆

Dialog with clients in the intelligence community indicates that cyber security professionals generally assume that their systems are vulnerable to infiltration or indeed that they have already been infiltrated to some degree. However, cyber security resources are limited, and the question arises of how those resources might be most effectively allocated to prevent or mitigate the prospective consequences of infiltration. Risk concepts provide a natural analytic framework in which to prioritize concerns, identify effective protective measures, and determine the optimal distribution of security resources. In numerous domains this set of methods and practices is generally referred to as risk management. To be sure, risk modeling has a history in the development of critical infrastructure such as nuclear power plants and industrial systems. Risk models have been successfully applied to cyber security to generate industry specific standards and certification programs. The cyber-attack risk inference model task examines existing risk management methodologies to determine their applicability to the cyber security domain.



The cyber-attack risk inference model.

The objective of this project is to provide methods to prioritize the responses available to a system administrator to minimize the potential consequences to the organization's mission. We are formulating a model that will provide a dynamic risk informed framework to prioritize the proactive protection of assets and mitigation of attacks already initiated, thus resulting in a basis for the effective use of limited security resources. This will be achieved through development of: 1) the analytic framework in which to characterize modes of cyber attack systematically, relevant protective systems, and potential consequence severities (in terms of the cost impact of compromised assets and disruptions to operational continuity), 2) a repository of attack scenarios identified through analysis, elicitations, and literature review, and 3) a means of risk quantification based on probabilistic or more recently explored non probabilistic methods.

During FY 2009, we evaluated candidate application domains on specific criteria and selected supervisory control and data acquisition due to project team synergies and alignment with mission outcomes. First, we defined model framework for calculating consequences and effects of mitigations, including a qualitative Bayesian network to model dependencies between mitigations and assets as well as a modified Dempster-Shafer used for a quantitative approach. We developed a data model for holding application domain specific knowledge. Also, we elicited and constructed a prototype model in the supervisory control and data acquisition domain. Shortly, we will have a framework for supporting a limited scope cyber risk model with an established structure containing an inventory of attack scenarios. The project scope will be rendered more tractable by limiting consideration to a specific cyber domain.

In FY 2010, the expansion of the repository of assets and attack scenarios will continue, and the prioritization methodology will be refined based on insights from this year's outcomes. Using standard software practice, we will create new risk models and validate these models against the opinions of subject matter experts. We will use empirical experimentation to verify the models and determine their effectiveness as well as examine the feasibility of using multi criteria optimization to prioritize cyber responses. Most importantly, we will provide the methodology to modify risk model parameters in response to real time events to alert cyber systems and administrators to changes in response prioritization.

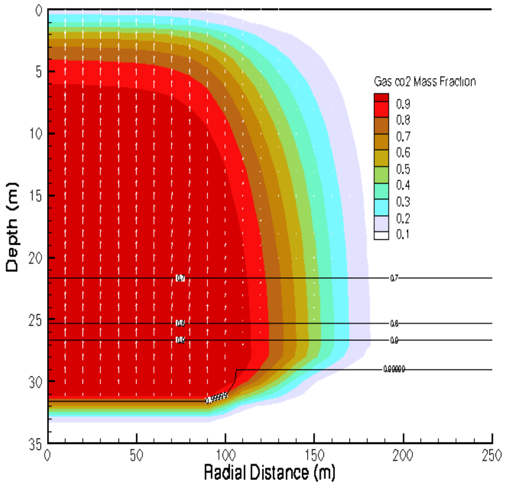
Developing a Generic Numerical Module for Simulating the Transport of Gas with Multiple Components for the Design and Safe Implementation of In Situ Gaseous Reduction Remediation

Zhuanfang (Fred) Zhang, Lirong Zhong, Mark D. White, Yilin Fang

◆ This project has developed an aqueous gas multicomponent operational mode for STOMP—the Subsurface Transport Over Multiple Phases—simulator to reproduce multicomponent gas transport and the chemical reactions between gas components and contaminants. ◆

A large amount of radioactive contaminants resides in the vadose zone of the Hanford Site and other areas around the country. PNNL has developed the in situ gaseous reduction remediation technology to immobilize redox sensitive contaminants, such as chromium VI [Cr(VI)], pertechnetate [Tc(VII)], and uranyl in the deep vadose zone using a diluted hydrogen sulfide (H_2S) gas mixture with N_2. However, the in situ gaseous reduction technology has not been used in Hanford or elsewhere due to DOE's concern about the safety of toxic H_2S during remediation.

In FY 2008, we developed an aqueous gas multicomponent operational mode as Water-N-components-gas-Energy (WNE) to simulate gas transport with one or more components in the vadose zone and coupled with the reactive transport module ECKEChem to simulate chemical reactions during the gas transport process. The developed code can be used to simulate the in situ gaseous reduction process, and recommendations can be provided for the optimal network design and safe implementation of the in situ gaseous reduction technique for deep vadose zone remediation. The code is also capable of simulating multiple components gas, especially those that contain CO_2 and CH_4, transport in a landfill, a CO_2 sequestration site, nuclear repository, and other subsurface conditions.



The distribution of the STOMP-WNE-simulated gas CO_2 mass fraction due to CO_2 leak from a 100 m radius sequestration site 30 m below ground surface.

During FY 2009, STOMP-WNE was debugged and tested for the newly developed input options (e.g., boundary conditions, source terms, initial conditions related to gas components) by comparing simulation results with those verified with the water-air-energy mode of STOMP (STOMP-WAE).

For simulations with STOMP-WNE, air was considered as a four component gas, the molar fraction of which are 0.2095 for O_2, 0.7808 for N_2, 0.0093 for Ar, and 0.0004 for CO_2. For simulations with STOMP-WAE, air was treated as a single component gas. The developed STOMP-WNE contains FORTRAN 77 static and 90 dynamic codes. Simulation results obtained with static and dynamic executables were compared. For the base test case, 56, 8, and 52 STOMP-WAE were compared with corresponding WNE variables in the OUTPUT, SURFACE, and PLOT files, respectively. Of the 116 variables, the relative difference was less than 1 percent for 110 variables, between 1 and 5 percent for four variables, and 17.4 percent for two variables (the gas diffusive water and gas diffusive air fluxes). These results indicate very good agreement between the two codes. As demonstrations, the code was also used to simulate the CO_2 leak from a sequestration site and CO_2/CH_4 transport in a landfill. The results were compared well with those in the literature.

An experiment of injecting diluted H_2S in N_2 into a column containing Cr(VI) contaminated Accusand was carried out to investigate the reaction between Cr(VI) and H_2S. A total of 292 g #20/30 Accusand containing 289 mg (5.56×10^{-3} mol) Cr(VI) and 1.34 %wt water was packed in a 30.4 cm long, 2.6 cm diameter column. The 200 ppmv H_2S in N_2 was injected at the rate of 240 ml/min while the inflow and outflow H_2S concentration was monitored. The experiment was terminated when the outlet H_2S reached the same concentration as that within the inlet, indicating that there was no H_2S soil consumption. After the experiment, the column was flushed with water for measuring unreduced Cr(VI). Results show that 1.48×10^{-3} mol of H_2S was consumed by the column, of which only 1.8 percent was consumed by Accusand. A leaching test performed after the gas reduction recovered 55.1 percent of the total Cr(VI) mass from the column. This result implied that under testing conditions, complete Cr(VI) reduction was not achieved when effluent H_2S reached 100 percent of the inflow concentration, indicating that the Cr(VI) reduction by H_2S is a kinetic process. Reduced gas mixture flow rate may increase Cr(VI) immobilization efficiency.

Development of Core Informatics Analysis Tools for Confident Protein Identification and Quantitation

Gordon A. Anderson, Gordon W. Slysz, Anuj R. Shah, Joshua N. Adkins, Brian H. Clowers, Navdeep Jaitly, Brian L. LaMarche, Anoop M. Mayampurath, Richard D. Smith

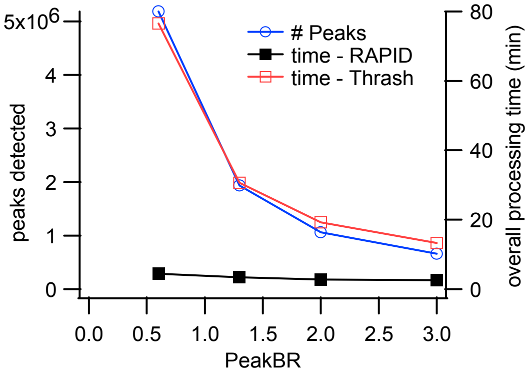
◆ An organism's proteome contains information about its condition, including stress indicators. Uncovering this rich data from biological samples takes high performance instrumentation and advanced software tools. This research will result in the next generation analytical tools to enable discovery of proteomics profiles. ◆

Identifying proteins in complex biological samples requires high performance, high throughput instrumentation. Typical workflows accomplish protein identification by combining liquid chromatography with mass spectrometry. This research added ion mobility, which affords another level of separation and includes the potential for more protein identifications and higher throughput. With this added capability comes increased volumes of data for processing. Currently, analysis tools are not available for the ion mobility dimension, and the benefits cannot be exploited without analysis tools to extract and identify peptide features from raw data using databases.

Our research developed advanced feature detection algorithms to expose and characterize the new dimension of information. Additional developments allowed these features to be identified. For example, a database of peptides and their ion mobility characteristics can be used to identify a feature found in raw data. To enable this capability, software tools were developed and existing tools embellished. We formulated the advanced analysis pipeline that will extract important information from raw data and enable biological discovery, helping to address vital issues such as bioenergy and carbon management.

In FY 2008, critical analysis capabilities were developed to enable high performance data analysis and proteomics samples identification. The focus of FY 2009 research was developing algorithms and techniques needed to extract useful information for the ion mobility/time of flight raw data. In order to use and fully test these techniques, we developed and expanded key tools with new capabilities.

Feature Detection Advances. Decon2LS operates at initial data processing to read raw mass spectrometry and sum/smooth data and detect peaks and isotopic profiles. This results in deconvolved mass and time data, which are then passed to a database for further examination. Decon2LS was initially developed for processing data from typical workflows that separated peptides using chromatography and high resolution mass spectrometry and has met our mass and time tag approach needs for several years. The addition of ion mobility as method for separating peptides required re-evaluation and modification of Decon2LS. Earlier versions relied on a framework that contained raw data reading, peak detection, and deconvolution algorithms. The new structure enabled an alternate algorithm (RAPID) without corroding the original DeconEngine codebase and reduced deconvolution by up to 40 times. We envision feed-backward loops from downstream processing that will enhance performance. The new Decon2LS framework provides the robust structure capable of supporting small and large changes to the manner in which peptide features are extracted.



Speed performance of typical deconvolution THRASH versus the alternative RAPID as enabled by Decon2LS framework. PeakBR represents a parameter within Decon2LS that filters noise peaks.

Peak Matching and Alignment. MultiAlign is an application that performs peptide identification via multiple alignments to a unique database. It can detect observed, unidentified features across multiple data via clustering. Our research resulted in several advances (alignment, visualization, large scale analysis tests and features, calibration refinement functionality, and confidence scoring) that will yield enhanced processing capabilities. The necessary frameworks are in place for peptide identification using ion mobility drift time, calculation, and large scale analysis.

In preparation for next generation platform and data analysis, we modified MultiAlign to handle data captured by the new platform, including ion mobility drift time. We have demonstrated the ability to load and handle such data output successfully from Decon2LS. We can now support advanced peptide conformer detection and identification using ion mobility drift time. In addition, we have modified the MultiAlign analysis pipeline to incorporate ion mobility data, thus enabling the use of drift time to return higher confidence peptide identifications.

Development of Exascale Algorithms for Molecular Modeling

Karol Kowalski, Eric J. Bylaska, Marat Valiev

◆ Our main purpose is to develop new modeling tools that can be effectively used on next generation computer architectures. In particular, we will significantly advance time and spatial scales of multiscale simulation methods and excited state methodologies. ◆

A wide range of molecular processes require highly diversified methodologies to describe systems characterized by different time and spatial scales. In a vast majority of situations, this problem entails a need for having multiscale methods built upon fundamental solvers whose scalability and accuracy define the final performance of combined approaches. Given dramatic increases in computer technology over the last decade, it is expected that exascale capability will lead to a significant shift in the system size and time scales. The progress in enhancing parallel performance of multiscale methodologies rests upon concomitant, balanced development of all constituent parts of a given multiscale approach. In the proposed research, which aims at the achieving scalability across 10^6 or more processors, this translates into designing novel upscale spatial and time methods, including automated, self consistent algorithms for securing new quality of inter atomic classical potentials (as well as its extensions to excited state simulations) and development of efficient multilevel time solvers in order to push the time limits for molecular simulations.

We propose to develop a fully automated, self consistent, and dynamical method to generate classical potentials based on smaller scale ab initio calculations done asynchronously and in conjunction with a classical molecular dynamics simulation. The proposed scheme has several advantages over conventional methods of generating classical molecular dynamics potentials. By providing a concise definition of the effective molecular dynamics potential, we will remove the ambiguity from choice of the fitting parameters or from the fitting process itself. It also guarantees that within a given functional form, resulting parameters will yield the best approximation to the full partition function of the system. Unlike the case of traditional empirical potentials fitted to a small set of equilibrium experimental data, different structural configurations will be sampled in the course of the calculation, leading to a better transferability of the resulting potentials. There is no restriction on choice of the functional form of potential (including grid or basis expansion), and new analytical forms better suited to model complex materials can also be explored under the proposed scheme.

During FY 2009, significant progress was made in several tasks on this project. A new coupled cluster excited state, non-iterative methodology based on the reduced iterative core was developed. In addition, a new parallel in time algorithm was implemented and tested on several benchmark systems, and a novel ground state coupled channel formalism was fully integrated with multiscale, multi-physics formalism. Preliminary tests clearly showed the scalability of newly developed ab initio codes across 6144 excited state coupled cluster methods and 20,000 hybrid density functional theory/molecular modeling approach central processing units. The reported parallel performance was demonstrated in contemporary excited state calculations for fused porphyrin dimer and hybrid density functional theory/molecular modeling approach calculations for 80 atom cell of hematite. Substantial improvements in speed, memory management, and communication pattern were achieved in the first year. Six papers reporting on this progress were either accepted or submitted in FY 2009.

For FY 2010, we plan to implement innovative parallel strategies based on the improved data flow for iterative electronic structure methods. In addition, the chosen non-iterative coupled cluster methods and ab initio molecular dynamics approaches will be adapted to the newly emerging graphics processing unit based computer architectures, which should significantly accelerate existing codes. We will also develop new parareal and fragment-based, multiscale, multi-physics methodologies. We will use the configuration interaction extension of the method of moments to achieve the desired level of accuracy. Also, we will clearly identify computational bottlenecks that can substantially affect the overall performance of the proposed algorithms. For the purpose of resolving these issues, we envision a close collaboration with several computational science projects. As such, we anticipate improvements in several key computational kernels.

Ultimately, our project will potentially have a long standing effect on the routine calculation performed on the next generation of computers. We anticipate a significant shift in both system size and accuracy level characterizing exascale molecular simulations. The expected outcomes of this project are computational chemistry algorithms that will be published in the scientific literature, including scalable, excited state approaches for exascale molecular simulations, the efficient interface between ab initio theories and mulitscale, multi-physics simulation module, and the exascale parallel in time algorithms (or parareal algorithms) integrated with terascale ab initio molecular dynamics and the terascale molecular dynamics programs.

Development of Gaming Technology for Cognitive Enhancement in Predictive Analytics

Roderick M. Riensche, Patrick R. Paulson, Gary R. Danielson, R. Scott Butner,
Lyndsey R. Franklin, Louis M. Martucci, Joshua Short, Nino Zuljevic

◆ This project aims to develop techniques and a systematic framework to enable the creation of a specific type of serious game in which the user collaboratively and competitively explores and selects plausible scenario outcomes using predictive computational models. ◆

As computational ability increases, models also increase in complexity, simulating an ever increasing range of physical and behavioral phenomena. Ultimately, human consumers of these model outputs must reason over implications, identify and mitigate risks and opportunities, and formulate and implement plans to capitalize on opportunities. We seek to streamline this entire interface, allowing human players to maintain an interactive role in the modeling process, tapping their creativity to facilitate better predictions of real-world behavior.

Today, the use of gaming as a mechanism to create stimulating user interaction with computer systems is widely recognized, as evidenced by the wide array of training games. In these training application games, content delivery and interactions are designed to stimulate the user's senses and enhance user experience by augmenting cognitive functions such as memory, attention, processing speed, and cognitive control. These games also present a natural environment for problem-solving. In many games, success is achieved by repeatedly solving similar but nonidentical problems; in others, players solve a specific problem repeatedly by doing so more quickly and efficiently. Previous work has acknowledged this concept, creating serious games for exploring possible decisions rather than focusing on training. These efforts have typically dealt with specific problem domains. We believe that a generalized approach can add value by making game-based approaches more accessible in modeling and analysis problems. In our project, we are maintaining the computational modeling and game software separately. While not seeking to create a purely generic game engine that could be plugged into an arbitrary computational model without modification, we are attempting to advance a unique method in that direction by developing a methodology and framework to facilitate easier application of gaming approaches to model outputs.

Work during FY 2008 involved three parallel efforts. For the first task, the game architecture supports the interface between results obtained from existing domain models and players interacting in a controlled, scripted environment. The architecture is intended to provide an abstract method for describing interactions between players and models. While the architecture does not prescribe a single game paradigm, it defines key ingredients of game configuration by which interaction between players and models are defined, including parameters, domain models, roles, elements, and handles (factors influenced by players). These are implemented in the prototype environment to provide end to end flow of information between players and data (model outputs). The second effort is used to facilitate experimentation with model interfaces. For this effort, we constructed a prototype development environment to implement the game ingredients. Finally, for proof-of-concept implementation, we began developing prototype games. We used a simple economic profit model for our first game definition, primarily to exercise our definition rather than fully developing the game. We also started to define a game configuration for a more complex domain dealing with climate change, biofuels, and national resilience.

During FY 2009, we continued developing the biofuels game, bringing it to partial completion where it could be "played" to exercise the framework implementation more fully. We also began developing the IED game, working with another technosocial predictive analytics modeling project. In developing the IED game, we explored integration methods with Bayesian network models and developed techniques for translating player actions into model "evidence" and provided feedback to players using modeled probabilities of event occurrence to control the feedback frequency and type. We defined mechanisms for capturing game data, leveraging our abstract game definition ingredients, and constructed a database to hold the IED game's recorded data. Finally, we began documenting the evaluation process to catalog and test specific analytic gaming propositions, including potential insights at three distinct development phases: game definition and model integration specification, game play, and post game analyses of recorded game data.

Simultaneously, we are defining a game configuration for a more complex domain dealing with climate change, biofuels, and national resilience. Future effort needs to focus on translating that configuration into a working implementation while refining our methodology and evaluating the effectiveness of the resulting game. With this in mind, we intend to refine the IED game during FY 2010 and use it for further evaluation and post game analysis work. We are also examining other types of model interfaces and techniques for allowing explicit interactions between human game masters and game driving models.

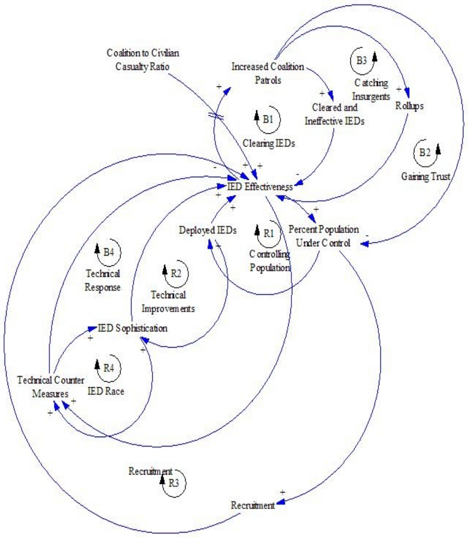
Dynamic Scenarios for Organizations in Infrastructures

Paul D. Whitney, Sandra E. Thompson, Katherine E. Wolf, Garill A. Coles, Jonathan Young,
Cynthia L. Henderson, Bonnie L. Hoopes, David A. Niesen, Kenneth D. Jarman, Stephen J. Walsh

◆ We will develop our generally applicable mathematical methods for real-world scenario modeling in the context of anticipating and countering terrorist attacks. This project will perform, examine, and publish a series of demonstration calculations of these mathematical modeling methodologies in each of the contextual settings. ◆

The ability to estimate the likelihood of future events based on current and historical data is paramount to government agency decision making, which currently relies only on individual judgment, experience, and instinct. If successfully accomplished, numerous predictive tasks, such as deterring weapons of mass destruction events, countering and characterizing risks associated with terror events, and understanding the effects of options for resource deployment, would have significant value. Accordingly, these predictive tasks involve technical and social components. We will leverage widely disparate computational modeling methodologies to support tasks integrated with relevant associated data and evidence to present decision makers with predictive likelihood estimates.

This project developed predictive computational modeling advances focused on two methodologies: system dynamics and Bayesian network models. System dynamics are a computational representation of flows, and Bayesian networks provide generalized quantitative modeling with methods for integrating data. We developed a method for linking these modeling modalities and formulating a quantitative calibration for Bayesian models. Technical advances focused on integrating information from the modeling approaches and associated data and evidence. Technical and social components will likely be known with differing accuracies; therefore, a critical challenge is linking across domains while respecting the fundamental difference in certainty level. With the rapidly evolving computational predictive social modeling, a major focus is on methods for validating and understanding information within combined models and data.



Primary constituents and feedback relationships among improvised explosive device clearings and deployments.

In FY 2008, we demonstrated how Bayes nets could combine social and technical models to perform data integration. We explored multiple model options for nuclear proliferation and terrorist threats (specifically improvised explosive devices). We developed representations and linkages between behavior and process (technical) models, scenarios, inferences, and examples. From a social/behavioral perspective, devices such as attack tools include numerous motivational elements challenging to model. We constructed a representation designed to incorporate generic threats (elements within the model relevant to devices, other forms of terrorist activities, or bad actors). The general ingredients of a scenario and examples include who (insurgency, religious, political extremists), what (explosive materials), where (geographic location), when (date/time, perhaps with a preceding observational event), why (desired outcome), and how (method of attack execution).

In FY 2009, we developed a method for calibrating Bayesian network models with organizational behavioral data. The data coverage for these models is incomplete; accordingly, methodology was required to accommodate initial opinions and sporadic coverage of the models. A Bayesian method of data augmentation was identified and implemented for accomplishing this calibration. This is a general approach for parameter estimation well-suited for Bayes network models. The methodology was demonstrated on a political radicalization model using data available from the Minorities at Risk database. The outcome was a significant change on prior parameter estimates for the Bayes network model of political radicalization.

We also developed methodology for linking system dynamics and Bayesian network models. Considering multiple methods simultaneously may improve this situation, but a better solution provides a framework for integrating different, potentially complementary modeling paradigms to enable comprehensive modeling, predictions, and thus better informed decisions. The primary challenges of this kind of model integration are bridging language and conceptual gaps between modeling paradigms and determining whether natural and useful linkages can be made in a formal mathematical manner. We applied model integration to technosocial models of insurgent led improvised explosive device attacks and security force countermeasures.

Exploring Architectures Suitable for Scientific Applications at Exascale Levels

Oreste Villa, Andres Marquez

◆ The aim of this project is to provide guidance to PNNL domain scientists on the refactoring and design of algorithms suitable for future exascale platforms. Current and future DOE applications will benefit from the ability to run faster and more accurately on large-scale machines. ◆

Given recent computer hardware design, it is likely that a future exascale system would contain hybrid processors composed of hundreds of cores and/or special purpose hardware accelerators. This project focuses on the evaluation of novel architectures that, in large-scale system configurations, can potentially achieve performance at exascale levels (1 billion billions of floating point operations/sec [FLOPS]). A recent promising trend in computer architecture design is stream processing, an execution paradigm that allows some applications to exploit parallel processing. Such applications can use multiple computational units (such as floating point) without explicitly managing allocation and/or communicating among units. One of the most common forms of stream computing is in graphic processing units (GPUs). Current GPUs are highly parallel multicore, multithreaded accelerators capable of performing general purpose computations. As accelerators, they must be interconnected through a CPU based host system. This project addresses the computational challenges involved in molecular simulations and subsurface flow and transport applications at PNNL.

NVIDIA GPUs are composed of 240 cores at 1.35 GHz and are able to achieve a theoretical peak performance of approximately 1 TFLOP in single precision and 90 GFLOPS in double precision. A cluster of GPUs of the same size as PNNL's Chinook supercomputer (2130 nodes) would achieve a theoretical peak performance of about 10 PFLOPS in single precision and 1.2 PFLOPS in double precision (as reference, Chinook has a peak performance of nearly 200 TFLOPS). Generations of GPUs in the near future are expected to have double precision performance comparable to single precision levels. NVIDIA GPUs are programmed using compute unified device architecture, a software for issuing and managing computations on GPUs. This architecture treats the GPU as a data parallel computing device without the need to map computations to the graphics pipeline explicitly. With standard C language, compute unified device architecture simplifies GPU based software development for scientific computing compared with previously used graphics oriented languages.

In FY 2009, we investigated the use of GPUs in the context of molecular dynamic simulations, a computationally intensive method used to study the time evolution of a system of atoms using Newton's classical equations of motion. One of the most time-consuming parts of molecular dynamic simulations is the computation of interaction forces, which usually takes more than 90 percent of the total simulation time. The force computation has to calculate the interactions between each atom in the system with every other atom, giving rise to $O(N^2)$ evaluations of the interaction in each time step. The interaction forces decrease rapidly with increasing distance between atoms. Thus, it is possible to neglect forces between atoms separated by more than a cutoff distance; therefore, atoms have interaction forces only with atoms in a sphere with a radius equal to the cutoff.

We implemented a functional and complete GPU enabled molecular dynamic simulator capable of calculating bonded and non-bonded forces between atoms of a periodic system. As reference, we implemented a multithreaded non-bonded force calculation on conventional CPUs to test performance and correctness of the GPU counterpart. On the GPU the computation of the interactions of each atom with the other N atoms (or less, depending on the cutoff) is performed by one single thread. Thousands of threads are mapped on the 240 cores of each GPU, such that a single core is responsible for calculating the iterations of several atoms with the rest of the N atoms. Having multiple threads mapped on the same computing unit allows hiding memory access efficiently, thus reducing overall execution time.

We tested the application on a system consisting of an AMD Phenom II CPU running at 3.2 GHz and 4 NVIDIA Tesla C1060 GPUs. Preliminary results for a 1 million atom simulated structure show a speedup of up to 300 times for the full application running in single precision without cutoff optimization on 1 GPU versus 1 CPU core. The speedup slightly decreases to 280 times for 4 GPUs versus 4 CPU cores. Enabling the cutoff the measured speedup was of 100 and 90 times, respectively, for the 1 GPU versus 1 CPU core and 4 GPUs versus 4 CPU cores. On double precision, the GPU code outperforms the CPU base code 15 times with cutoff and 10 times without cutoff. Thus far, results are encouraging, and we expect further performance improvements as development progresses.

During FY 2010, we will develop working compute kernels on select multi/manycore architectures using real data sets. We will also investigate performance refinement and evaluation of the kernels, worst case execution timing, corner case analysis, comparison of programmability efforts, and power consumption.

Fundamental Investigations of Heterogeneous Catalysis Using Computational Methods

Donghai Mei

◆ This project aims to enhance the applications of revolutionary and new sources of energy by developing multiscale computational capabilities for the rapid discovery and rational design of new catalysts and elucidation of reaction mechanisms of catalytic hydrogen production. ◆

Heterogeneous catalysis plays an essential role in creating new routes and flexibility in the network of energy sources, carriers, and conversions. Effectively combining quantum chemistry, computational methods, and statistical thermodynamic and dynamical theories for modeling chemical reaction kinetics on catalyst surfaces that can directly compare with experimental measurement is important. Two computational modules, first principles based kinetic and adaptive kinetic Monte Carlo simulations, have been developed under this project.

This project will develop and apply computational capabilities at PNNL to probe catalytic reaction mechanisms and kinetics bridging from the atomic to the macroscopic level. The core capabilities developed under this project, a kinetic Monte Carlo module and a module for identification of probable elementary reaction steps will enable a theoretical description of heterogeneously catalyzed processes in which numerous elementary chemical reaction steps compete with each other at active sites on various catalyst surfaces. The uniqueness of our development lies in a generic kinetic Monte Carlo module widely applicable to catalysts with varied, well-defined surface structures and compositions. Moreover, we will develop a module to facilitate the identification of probable elementary reaction steps and that captures recent methodological advances in modeling of "infrequent events." These new computational modeling tools will enable us to ascertain reaction mechanisms, provide quantitative kinetic rate parameters for elementary steps, and allow evaluating performance of catalysts on multiple scales. The power of these two new modeling tools will be demonstrated on three catalytic systems relevant to the hydrogen economy and that share common transition metal catalysts and elementary steps: water gas shift, preferential oxidation of CO in the presence of excess H_2, and steam reforming of small oxygenates.

During FY 2009, we applied first principles-based kinetic Monte Carlo simulation to study ethanol synthesis from biomass derived syngas on silica supported Rh/Mn alloy catalysts. On the basis of first-principles density functional theory calculations, we found that the alloying of Mn into Rh metal particle is critical to improving activity and selectivity toward ethanol and other C_2^+ oxygenates. Although doping Mn into Rh will not dramatically change activation energy barriers to methane formation, it will lower the barrier of CO insertion into CH. The kinetic Monte Carlo simulation results are in qualitative agreement with experiments and previously reported data, indicating that the newly developed simulation model in this project captures the essential chemical and kinetic features of ethanol synthesis over the supported Rh/Mn catalysts.

Also in FY 2009, we used the adaptive kinetic Monte Carlo method to calculate the dynamics of methanol decomposition on Cu(100) at room temperature over a time scale of minutes. Rates of reaction were calculated with harmonic transition state theory. The dynamics followed a pathway from CH_3OH, CH_3O, CH_2O, CHO, and finally CO. Our calculations confirm that methanol decomposition starts with breaking the O-H bond followed by breaking C–H bonds in the dehydrogenated intermediates until CO is produced. The bridge site on the Cu(100) surface is the active site for scissoring chemical bonds. Reaction intermediates are mobile on the surface which allows them to find this active reaction site. This study illustrates how the adaptive kinetic Monte Carlo method can model the dynamics of surface chemistry from first principles.

The morphology of oxide supported noble metal clusters has been one of most important issues in heterogeneous catalysis. In collaboration with another LDRD project, various structures extracted from optimized tetragonal Pt_xO_y bulk and the adsorption structure of PtO monomers at full monolayer on the γ-Al_2O_3(100) surface were investigated. We found that the most stable PtO structure is the O-terminated two-dimensional PtO(101) raft overlayer structure, which strongly interacts γ-Al_2O_3(100) surface via four O-Al_V bonds on a γ-Al_2O_3(100) surface. This is consistent with our ^{27}Al nuclear magnetic resonance and high-resolution scanning transmission electron microscope measurements. Density functional theory calculations performed in this work unambiguously confirmed that the pentacoordinated Al sites on the irreducible γ-Al_2O_3 surface play an essential role in anchoring two-dimensional PtO overlayers under the oxidizing environment. The strong interaction between PtO overlayer and the (100) orientation surface of the γ-Al_2O_3 due to the existence of unique pentacoordinated Al sites indicates the shape and dispersion of the metal cluster can be controlled by the modification of metal oxide substrate. This work has been published on *Science*. Once again, concerted efforts that combined experimental investigation and theoretical modeling with this project prove the best approach to strengthening our capabilities of the PNNL catalysis research program.

Geological Sequestration Software Suite Core Architecture and Simulation Framework

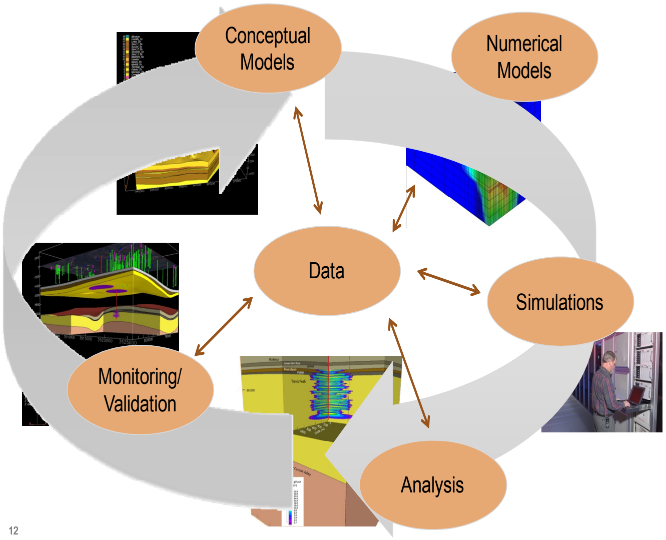
Ian Gorton

◆ Our geological sequestration software suite (GS^3) is a set of research tools that have been integrated through a software framework that streamlines the modeling process used to evaluate and monitor carbon dioxide sequestration sites. The software architecture components of the framework will be selected to meet the needs of usage so that a full production modeling environment can be deployed. ◆

Geologic sequestration is a technology currently being developed to mitigate global warming through the long-term storage of greenhouse gases. Finding suitable subsurface (underground) sites for sequestration of greenhouse gasses requires performing extensive studies that include modeling the site geology and evaluating the processes that determine the fate and transport of injected gasses. Subsurface modeling is an iterative process that can often take months or even years to complete and is continually revisited as new information is gathered. In addition, work is performed by interdisciplinary teams comprised of geologists, hydrologists, engineers, geochemists, and computational scientists who are unlikely to be co-located.

We are building a framework that incorporates off-the-shelf tools with which many modelers are already familiar; facilitates the creation/integration of new custom tools, utilities, and scripts; and integrates seamlessly with data management capabilities, including provenance capture and user annotation. We are working with carbon dioxide sequestration experts to prototype this framework in the context of two alternative candidate sequestration sites and identify data and tools needed to characterize and model these sites. Our specific contribution will be in the deployment of data management services, standardized formats, data translations, automated computational job management, and the component integration framework.

In this project, we have been working extensively with scientists to understand the modeling and simulation process for carbon sequestration. As depicted in the figure, this process involves multiple tasks that follow a loose, highly iterative workflow. Based on elicit requirements, our designed prototype software tool contains a highly flexible and extensible underlying software architecture. Thus, during FY 2009, we spent considerable time gathering requirements from geo-scientists and proceeded to design and prototype a reusable, extensible software architecture based on satisfying those requirements.



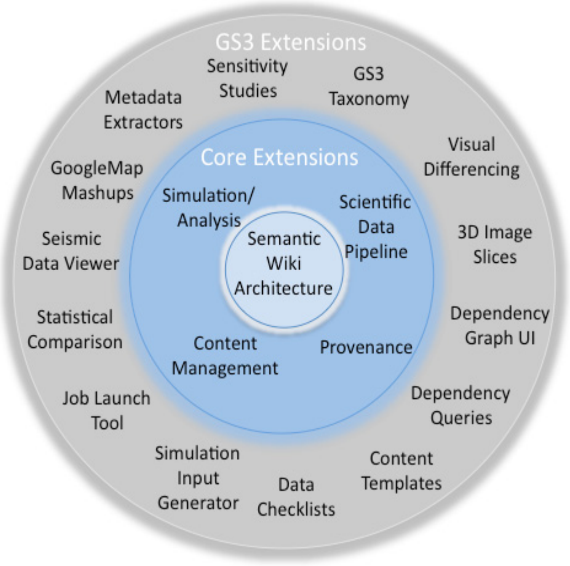
Overview of the subsurface modeling process.

Collaboration through data and knowledge sharing is a driving force behind our architecture, as is the goal of providing infrastructure that enables a self-sustaining community. For this reason, we specifically chose wiki technology for the core of our project and GS^3. Most wikis provide a rich web application development platform and a mechanism to add plug-in modules that operate on the wiki content. Of particular interest for GS^3 are the semantic extensions that enable a range of dynamic views of the content.

During FY 2009, we designed and built a prototype version of GS^3 and demonstrated it to various groups involved in carbon sequestration. The software adopts a novel layered architecture (as shown in the circular graphic) that enables it to be highly customizable for generic modeling and simulation environments. Based on our experiences thus far in the validation of our prototype, the following is an assessment of the architecture we have developed:

- The GS^3 environment is an excellent match to a scientific user base in terms of usability. Scientists are familiar with the underlying approaches that make collaboration and sharing of models and data seamless endeavors, even for geographically dispersed teams.
- The auto-generation of useful content leads to a consistent look and feel for the environment. Semantic queries are straightforward to create; hence, we can quickly modify the site in response to user requests.
- Provenance and model versioning provide an appropriate, lightweight solution for keeping track of the complex modeling process. When fully realized in GS^3, provenance has the potential to transform modeling practice by providing unprecedented data and quality assurance

levels for modelers who are simulating sites for carbon dioxide injection. In addition, these features allow scientists to use their desired modeling tools and store the resulting models and data in GS^3 for archiving and sharing.



A conceptual view of the GS^3 architecture. The core contains a semantic mediawiki environment surrounded by extensions for scientific data management and processing. The outer ring includes representative functions and capabilities tailored specifically to the geologic sequestration community.

- The ability to build the reference catalog incrementally under user control is well received, and the automated knowledge extraction pipeline makes the process simple for users. Developing semantic queries to create custom content pages is challenging for users, however, and we intend to create a simplified capability for this as a wiki plug-in.

We visited the national laboratories at Los Alamos and Lawrence Berkeley to present GS^3 to their geo-sciences groups. Feedback from these presentations provided excellent guidance on new features that we could viably build as well as a confirmation of the appropriateness of our approach.

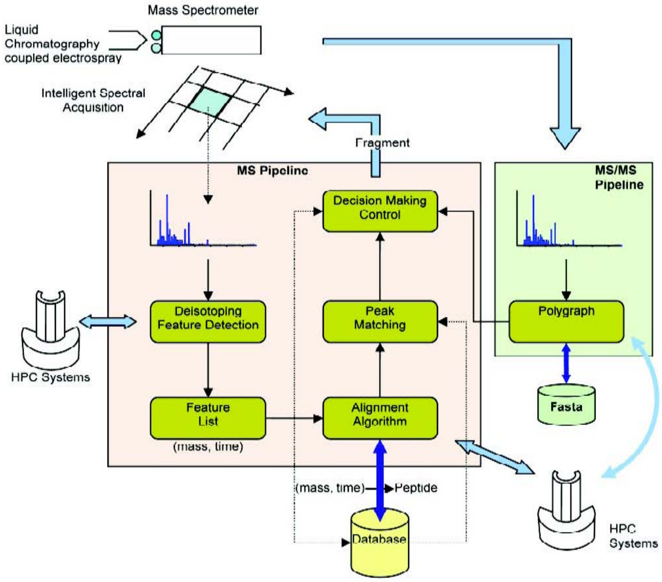
In FY 2010, we will fully define the conceptual data model and management from which we will create and integrate tools to transform the conceptual to numerical models to STOMP inputs for simulation. Other goals for this project are to develop data access tools for searching and versioning while solidifying user process tracking to enable process verification, audit, and provenance. Additionally, we hope to integrate visualization tools (e.g., Tecplot) and eventually demonstrate a more complete end-to-end framework prototype. Throughout the project, we will continually validate our approaches with users from the carbon sequestration modeling community to secure the enduring utility of our technologies.

High Performance Data Analysis Pipeline for Online Smart Mass Spectrometry

Anuj R. Shah, Andrei V. Liyu, Nino Zuljevic, Matthew E. Monroe,
Ashoka D. Polpitiya, Joshua N. Adkins

◆ Data collection and analysis from multiple sensors generally result in an over collection of prominent data items, while underrepresented items may be ignored. We are developing an online analysis pipeline to control sensors in an automated manner to maximize the information content generated during a particular event and potentially reduce the number of events required to generate a comprehensive detection database. ◆

Independent, greedy collection of data events using simple heuristics often results in massive over sampling of prominent data features in large-scale studies over what should be achievable through intelligent, online data acquisition. As a result, data generated are more aptly described as a collection of a large number of small experiments rather than a true large-scale experiment. In this study, we will develop an intelligent online control and analysis system to enhance significantly the information content from each sensor; in this case, a mass spectrometer. Using online analysis of events as data are collected and decision theory to optimize the collection of events during an experiment, we aim to maximize the information content generated during an experiment by using pre existing knowledge to optimize the dynamic collection of events. Through this system, we will reduce the number of analyses in constructing a comprehensive detection database from thousands of possible experiments, each with over 10,000 detection events, to only tens. The computational system we develop will provide an order-of-magnitude improvement in processing time required for the offline analysis of otherwise redundant events. The system will be designed with scalability in mind so that intelligent collection events can be used simultaneously to guide not just one but several coordinated instruments.



High-performance data analysis pipeline for intelligent mass spectrometry.

In FY 2008, the middleware for data intensive computing integration (MeDICi) integration framework was incorporated within the application to manage data transfer and processing activities between the instrument and individual processing components. To support the framework, the de-isotoping algorithm was modified to work online in real time as opposed to offline, in which available data were collected prior to processing. Also, a small scale scheduling program was written to enable connecting multiple instances of the de-isotoping algorithm in the pipeline. This accomplishment resulted in the identification of new requirements for the underlying MeDICi architecture. We expect the MeDICi team to incorporate provisions for resource management directly into the integration framework, as opposed to burdening system users.

In FY 2009, we made further progress in identifying and developing the individual processing modules of the overall analysis pipeline. Specifically, we collaborated with the developers of a fast, efficient online data processing algorithm capable of de-isotoping data within the time constraints. We developed a central control software module that includes visualization capability of real time spectra and control commands for other software modules within the framework. Current functionalities include visualizations for data received from the mass spectrometer and visualization for the results of the de-isotoping process. We developed simulation modules that mimic the entire experimental procedure on a real time mass spectrometry, and results from this simulation software confirmed the impact this capability will have on the mass spectrometry community.

The results of our FY 2009 project work included delivering a poster presentation at the American Society for Mass Spectrometry Conference in Philadelphia, PA and presenting discussions about this high performance data analysis pipeline in a book chapter to be published in 2010. In addition, we presented a paper at the Institute of Electrical and Electronics Engineers e-science 2009 International Conference in Oxford, UK.

Hybrid Computing Solutions Applied to Feature Extraction, Characterization, Classification, and Clustering

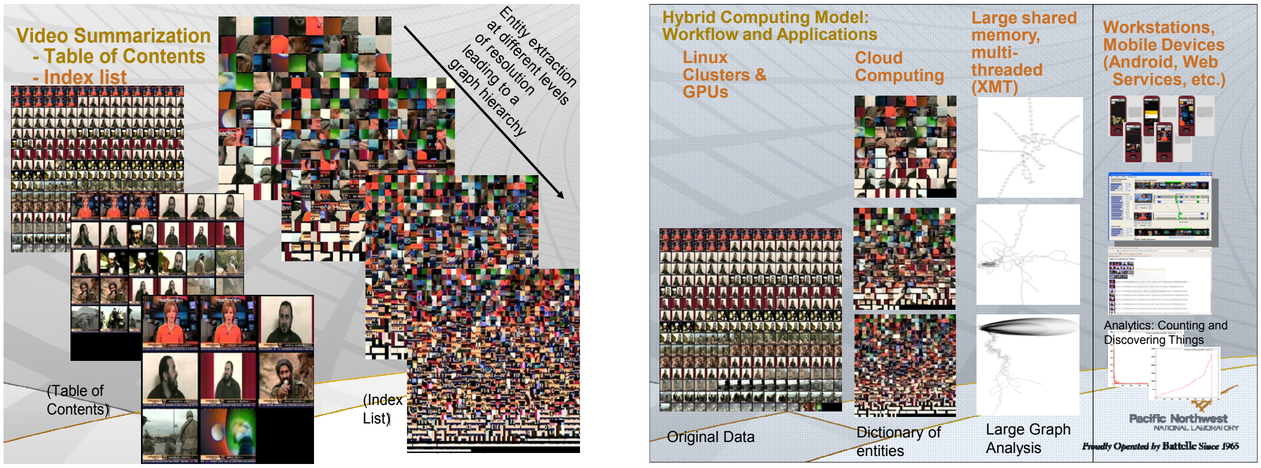
Harold E. Trease, Adam S. Wynne, Andrew J. Stevens, Ronald C. Taylor,
Lynn L. Trease, Brett G. Amidan, Paul E. Keller

◆ With the explosion of digital information generated from a multitude of sensor platforms, along with the inability of the computer industry to keep pace with Moore's Law scaling of computer chip clock speed, power dissipation rates, and communication bandwidth requirements, our whole computing infrastructure is being disrupted with a trend toward multicore computing hardware platforms. New algorithms, software implementations, programming models, and software infrastructure designs must be explored to determine how best to apply these configurations to solve data intensive applications. ◆

The production and use of massive amounts of unstructured video data are increasing for applications ranging from wide area, security surveillance, and large data repositories of archived video databases. Providing a software infrastructure for indexing, searching, and analyzing massive amounts of video data presents many technical challenges, including how to handle the ingestion of data from multiple real time streaming sources (e.g., unmanned areal vehicles or security surveillance systems at 100s to 10,000s plus) or storing and analyzing massive archived databases. Without automated, high throughput analysis tools, most captured video data may be stored and archived but never analyzed or processed because there just aren't enough eyeballs and time to watch it all, except in forensic contexts where a critical event occurs that requires specific segments of video to be examined.

Because of recent innovations in high performance computing architecture design, software developers now have a myriad of platform choices on which to implement parallel algorithms. Each architecture design lends itself to particular types of problems because of the specialized features and capabilities it provides. If the correct architecture and algorithm are chosen for a given task, the developer can achieve near optimal performance. However, solutions to real world, data intensive problems require multiple processing stages, each of which may have algorithmic characteristics lending them to different computing architectures. Therefore, it is expected that hybrid solutions combining the benefits of multiple platforms will play a large role in the high performance computing landscape of the future.

For this project, the effective use of heterogeneous machine architectures on different phases of a computational workflow for processing streaming and/or archived unstructured sensor data was demonstrated (e.g., surveillance video data is a good example of such data). This approach will demonstrate the advantages and/or disadvantages of programming, throughput, and hardware capabilities of each of the architectures. The hybrid architecture consists of a Nvidia GPGPU cluster, an IBM BE Cell computing cluster, a multi threaded, shared memory Cray XMT, a Netezza data warehouse, and a Linux cluster to extract/recognize features, perform clustering, and graph analysis using unstructured data. The results of the data extraction functions are high dimensional digital signatures placed into databases and transformed into large graphs to



At a high level, the configuration above contains: 1) a hardware network of modern multi core processors connected over a high speed interconnect, where hardware components are physically separated by hundreds of miles, 2) a control flow network controls major network workflow components, 3) a pipelined data flow network manages raw and processed video data flow throughout the network, and 4) a communication network to manage the messages passed between the network (master) nodes and cluster (slave) nodes, where messages may contain both data and functions.

extract relationships from the data. Processes running on each platform and the data movement between these hybrid hardware components will be coordinated by Middleware for Data Intensive Computing (MeDICI) architecture.

We explored the hardware design, algorithm design/ implementation, and performance/scaling of a hybrid multicore computer configuration applied to the solution of a pipelined application workflow for processing large quantities of unstructured image/video data. In general, image/video data represents a very bulky, low information content media. The major workflow steps involved in processing is data include the following: 1) importing, ingesting, and decoding all of the data, 2) running information processing algorithms in order to generate high dimensional digital signatures, 3) generating the sparse representation of the data, and 4) generating/performing graph analysis to extract relationships. The MeDICi architecture may be used to manage workflow across the different hybrid computing platforms. The results of this project demonstrate the utility of applying hybrid computing approaches to the analysis pipeline of data intensive applications such as real time streaming or archived data to generate sparse representations to provide indexed, searchable data structures and enable the discovery of data complex interrelationships.

During FY 2008, we assembled a hybrid, multicore computing network that consists of the following components: a Linux cluster (Grove), an IBM BE Cell (PS3) cluster (Mercury), an Nvidia GPGPU cluster (Frank), and a Cray XMT (Cougar-XMT). These machines were connected to a network topology using three software communication layers: a control network that directs the workflow, a flow network that communicates data, and a point to point message communication network for both functions and data. All network nodes are distributed across geographic locations, thus making Internet communication bandwidth a critical component. The controller, cell, and Nvidia clusters reside at the main PNNL campus in Richland, WA, while the Grove Linux Cluster resides at PNNL's Seattle office.

The previous year's work shows implementation of a video processing and content analysis workflow mapped to a distributed network of multi core processors. Each workflow component represents an optimal implementation on a given architecture. Because each multicore processor has its own programming language/extensions and optimization strategies different from other architectures, the code development process must be highly organized. Applications supported by the work presented include processing data from many (100s, 1000s, 10,000s+) surveillance cameras and processing archived video data from repositories or databases. The speed of this system ranges from 1 DVD/sec (5 Gb/sec) on Linux clusters to 500 Gb/sec (for the PCA analysis on a modern Nvidia GPGPU multithreaded cluster using only 4 GPGPUs). These numbers demonstrate a much greater than real time processing rate for the framework. Although throughput of the application within the processing nodes of is high, the overall throughput of the hybrid, multicore framework is limited to 137 frames of video/sec because of the 1 Gb connections between the machines.

During FY 2009, we created a video processing workflow that included a Linux/GPU cluster, a cloud computing component, the Cray XMT, and several clients, including a mobile Android platform. These machines were connected into a pipelined, geographically distributed network topology for processing video data. We continued to implement MeDICi as a workflow manager across the hybrid computing framework and performed optimization of the algorithmic kernel for each component of the framework. Also, we continued to develop the implement large sparse graph exploration algorithms on the Cray XMT and developed and optimized the algorithms on the Nvidia GPGPUs. After running performance benchmarks on the algorithmic kernels on their respective platforms, optimization strategies were captured and documented.

The major results of this project include: 1) the successful mapping of a complex workflow for video analysis onto a hybrid, multi core computing platform, achieving near linear scaling in performance for several of the individual pipeline steps (particularly the PCA on the Nvidia processors), 2) an initial mapping of the video workflow using a pipelined MeDICi implementation, and 3) publishing several papers and making conference presentations that describe in detail the implementation and performance/scaling results for this hybrid, multicore framework. The results demonstrated the utility of applying hybrid computing approaches to the analysis pipeline of data intensive applications, such as real time streaming or archived data to generate large, sparse graphs to discover interrelationships in the data.

The algorithms developed on each hybrid computing platform will be encapsulated by MeDICI constructs to produce processing components that can be manipulated and coordinated by a graphical workflow tool integrated with other independently developed components and re used as necessary. For data analysis, visualization tools such as the Digital Data Analysis ToolKit will be used to display the results. This project will demonstrate the effectiveness of a hybrid high performance computing solution by integrating the respective benefits of the multi core Nvidia GPGPUs, IBM BE Cells, and a multithreaded, shared memory Cray XMT machine using the MeDICI architecture to solve data intensive, unstructured data analysis problems.

Intelligent Compression and Data Organization for Multidimensional Data Volumes

Nathaniel Beagley, Chad Scherrer, Yan Shi, Brian H. Clowers

◆ A significant challenge in processing and analyzing the large data sets generated by scientific experiments is how to capture, store, and then access the raw data efficiently to perform the desired analysis tasks. This research aims to enhance scientific discovery through efficient data management and access specifically targeting improved storage and analysis by using data compression. ◆

A major problem with creating and analyzing large quantities of experimental data is how to capture and store the raw data and then access it for analysis. Often, the strategy is to store only parts of extracted features from the data, but this approach can lead to having to re-run expensive experiments. Another solution is to store the data in a compressed form, which decreases both the storage space and the time needed to write the data to disk. However, accessing the data becomes more cumbersome, leading to decreased efficiency in many analysis tasks.

To address the storage of and access issues with raw data files, our project proposes an indexed data compression scheme focused on the analysis of multi-dimensional volumes. Indexing information will enable specific subsets of the raw data to be extracted without decompressing the entire file. Additionally, to increase retrieval efficiency, data will be organized in the compressed file in an orientation most useful for the desired analysis task. The analysis algorithm (or user) can then perform a series of extractions on demand of the specific pieces of information required for the analysis in real-time. In particular, analysis tasks performing cross-sample comparisons will become significantly more efficient. The end result will minimize data storage requirements while maximizing the rate at which information can be retrieved and processed from multi-dimensional data sets.

In FY 2008, we designed, implemented, tested, and optimized an indexed compression scheme for data produced by ion mobility spectrometry (IMS), a data-intensive application area with instruments producing hundreds of megabytes per second. The data needs to be stored without any loss of data resolution. Additionally, the instruments have close to a 100 percent 24-hour duty cycle, potentially producing terabytes of data every year. Our storage solution had to be computationally efficient to allow compression and storage in near real-time and provide a large reduction in data file size to reduce, as much as possible, the load on the data storage infrastructure.

During FY 2009, multiple compression algorithms and strategies were tested. Each was evaluated on the computational time/compression size tradeoff as it applied specifically to the IMS data set. The final optimal algorithm is a two-pass method that runs a run length zero encoding algorithm (RLZE) over the data, followed by compression via the Lempel-Zif-Free (LZF) compression algorithm. RLZE is a custom adaptation of the run length encoding (RLE) algorithm, which is fast and leverages specific characteristics of the IMS data set to optimize compression size. LZF achieves compression sizes similar to GZIP in about a quarter of the time. The two algorithms applied in succession achieve a fast computation time that not only keeps up with the rate of instrument data generation but also allows capture of a higher data resolution from the instrument.

Compression size from our algorithm is optimized within these time parameters and provides a 99 percent reduction in size compared with the raw data's 60 percent plus reduction compared with the status-quo data storage format. The compressed data is indexed, allowing direct extraction of uncompressed data segments and providing increased efficiency in analysis workflows.

Our algorithms have been integrated into a real-time, data capture, and analysis environment for IMS data. Our compression methodology is also a key component to the unified ion mobility, PNNL's new format for storing IMS data. We also are exploring applications of this work to other large-scale scientific domains, specifically climate science. The project's resulting technology can potentially save large amounts of money and time in data storage and access and facilitate scientific discovery through improved analysis efficiency for proteomics and a wide range of other scientific domains.

	Raw Size	**Size with Zeros Removed**	**Compressed Size**	**Improvement (% Reduction)**
Low-Density IMS Data	240 MB	8.2 MB	3.1 MB	62.2
High-Density IMS Data	240 MB	89.9 MB	35.3 MB	60.8

Compression results from IMS of two different densities. A factor of three compression rate was achieved.

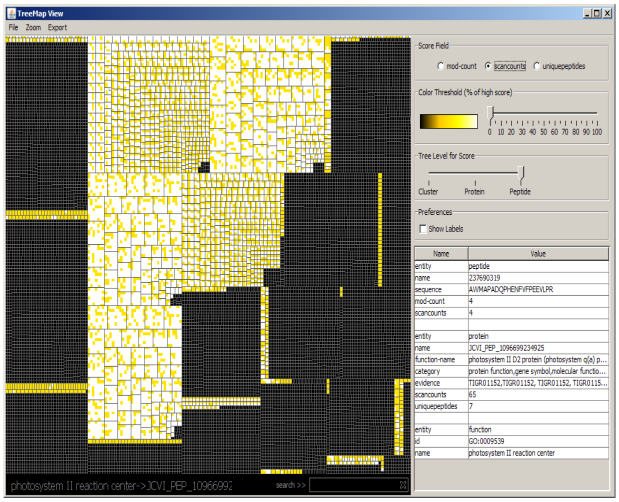
Interactive Visual Content Analysis of Real-Time Data Streams

George Chin, Natalie A. Freeman-Cadoret, Vidhya Gurumoorthi, Grant C. Nakamura

◆ Scientists and analysts need to comprehend and act efficiently and effectively on the meaning and context of streaming heterogeneous data in real time. To facilitate human understanding of high-volume, real-time data, this project will develop interactive visual content analysis capabilities and tools that may be attached to various real-time data streams and allow scientists and analysts to grasp the content, context, and organization of the streaming data quickly and intuitively. ◆

In visualizations, real-time data streams have multiple challenging characteristics compared with static data. Real-time data are dynamic, transient, temporal, and are created in massive volumes. Effective visualizations must accommodate this abstract and dynamic behavior and present it in ways that make sense and are usable to humans. The general strategy of this project is to develop and evolve visual contexts that will organize and orient complex dynamic data in conceptual and perceptive views. Relevant contexts include temporal, categorical, hierarchical, spatial, and geospatial. The goal is to allow users to grasp dynamic data quickly in intuitive, natural forms without requiring intensive training in the use of specific tools.

Many effective traditional visualization techniques already exist for analyzing static data. Various techniques for visualizing time-dependent data have also been developed. An aspect of our development strategy is to identify robust visualization techniques and evolve them to support dynamic, high-volume, real-time data. Useful modifications to existing techniques would include capabilities to connect to real-time data streams; store massive amounts of data; reduce, filter, and detect features in data to support data navigation and exploration; and view and analyze dynamic data behavior.



Score Field: ○ mod-count ● scancounts ○ uniquepeptides

Tree Level for Score: Peptide

☐ Show Labels

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Dynamic TreeMap tool showing protein and peptide patterns in sea sediment data.

This project is prototyping an interactive visual content analysis environment that will provide a suite of dynamic visualization tools. The tools will deploy abstract graphical representations that will be immediately meaningful to users and connect to high-volume, real-time data streams to provide immediate visual analysis support. The tools and environment will integrate multiple visual contexts, support multiple multimedia types (e.g., text, binary, video, etc.), link to other statistical algorithms and analysis tools to enable interactions, and be deployed within the middleware for data-intensive computing (MeDICi) framework to provide general visualization support for MeDICi applications.

The project's main FY 2009 contribution is the development of dynamic visualization prototypes: the dynamic spiral timeline allows scientists to identify periodic temporal patterns; the Dynamic TreeView and TreeMap allow scientists map dynamic data to hierarchies, taxonomies, and categories; and the Dynamic GraphView enables scientists to view transitions in the structures and relationships of changing data. Achieving rapid, efficient human cognition is a critical objective of these tools, as there are instant connections to the user's mental model of the problem, data, and the data's changing behavior. These prototypes fulfill the project's goal of developing innovative visualization tools that facilitate immediate comprehension and rapid visual analysis of dynamic data.

To validate the usefulness of the tools and concepts, we collaborated with scientists and analysts to evaluate the visualization tools against different types of intelligence, cyber security, biology, and proteomics data. In one particularly in-depth effort, we collaborated with microbial proteomics researchers to analyze protein communities in sea sediment collected from the ocean floor. The samples were collected over time into over 300 datasets, yielding 43 million proteins needing characterization and analysis.

Visual analysis capabilities were adapted and applied to support the ocean community proteomic research. Specifically, Dyanamic TreeView and Dynanic TreeMap were extended and applied to map the 43 million proteins against taxonomies or hierarchies emerging from hierarchical clustering algorithms. Using these tools, researchers visually identified protein and peptide patterns that they were unable to discover through other analyses.

Knowledge Encapsulation Framework

Andrew J. Cowell, Michelle L. Gregory, Keith Fligg

◆ The aim of this project is to develop a collaborative information analysis and discovery environment. The purpose is to enable end users to comprehend information resources they already have through semantic linkages and visualization and discover related information from traditional and social media. ◆

A knowledge encapsulation framework (KEF) is a collection of components aligned to produce novel information analysis environments. The core project work is based around a natural language pipeline, a semantic wiki environment, and numerous software components that can customize the wiki for particular uses. We focused on supporting modelers and their information requirements working on climate and security in the Indian subcontinent and improvised explosive devices in theatres.

A suitable metaphor for the capabilities provided by this environment is of an automated research assistant. Consider a piece of software that can take information important to a task (for modelers, typically journal articles, conference papers, technical reports, etc.) and place the material into an environment of team members. The environment "understands" what colleagues find interesting about the shared material and can query traditional media sites (academic portals, news sites) and social media (blog search engines), bringing relevant hits into the environment for approval. After the material is deemed useful, it becomes part of a growing collection of information resources. Finally, reviewing the collection and marking text as relevant to certain parts of the model, the system collects pieces like a smart notebook, enabling a parameterized model node. In some cases, the environment may even run models and present results to for review.

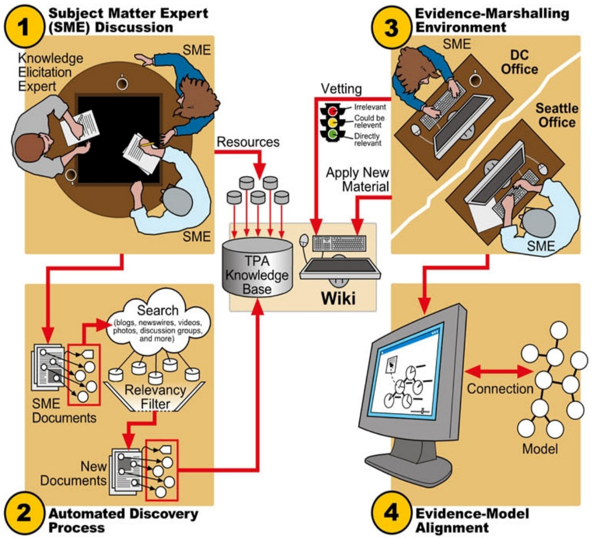
KEF enables this vision through several components. The core environment is a special kind of wiki with a semantic layer that allows users and software components to define relationships in text. For example, humans understand population statements but computers need to be told there is a property called *population* related to geographical locations expressed as a number. Having an environment express these relationships is the first step in structuring the masses of unstructured data that modelers (and many other analytical users) deal with. Having this information in a structured format allows for contextually correct visualization mechanisms (locations displayed on maps, times on a timeline, etc.).

We built a natural language pipeline through which all textual information passes on its way into the environment. The pipeline extracts text from other file formats (e.g., .doc, PDF) and performs entity extraction (identifies people, places, things, events, and groups), topics, sentiment (how people feel about a topic), and rhetoric (what people are saying, to whom, and for what reason). These are passed to the environment as properties so users can pose queries such as "show me all documents that include Paris (as a location) and climate change (as an event) discussed negatively." Such an environment provides data selection beyond what traditional keyword search systems can provide.

The environment can also bring new items to its users' attention. By allowing users to select documents in the environment as "seed" documents (documents important to research rather than of general interest), the system captures a subset of the properties (author and topic) and submits that as a search term to a data source (Google Scholar, Technorati Blog Search). Hits are evaluated for relevance using a term document frequency metric; those found to be beyond a specified threshold are discarded. The results are inserted into the pipeline and processed as above, retaining a provisional status until the information's usefulness is confirmed.

A focus of FY 2009 work was developing a tight linkage to models. This wider workflow from information identification to parameterizing resulting model nodes provided an effective environment. We placed considerable effort on the user experience to make the environment usable and compatible with other tools. Finally, we made a number of changes to the natural language pipeline, enabling new annotators to be attached easily for different missions.

For FY 2010, we will increase the environment's intelligence by looking at machine learning approaches to identify what elements of information are important for particular users. With this functionality, the environment can suggest and prioritize documents without requiring the user to read all possibilities.



The KEF collaborative information analysis process.

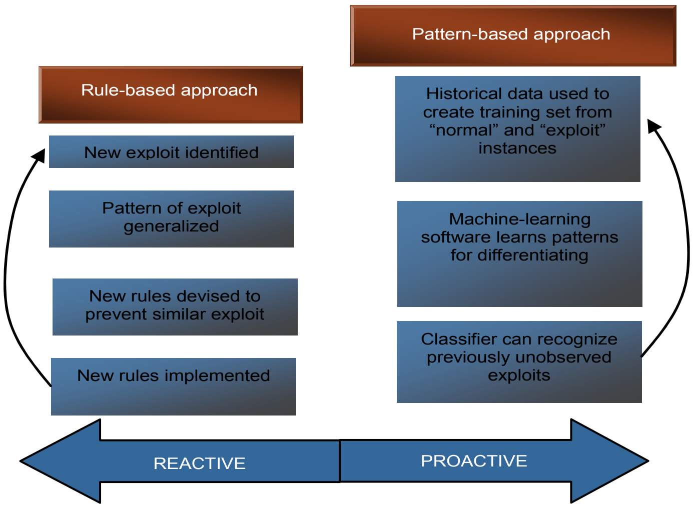
Machine Learning String Tools for Operational and Network Security

Christopher S. Oehmen, Bobbie-Jo M. Webb-Robertson, Patrick J. Nichols, William K. Nickless

◆ The goal of this project is to move toward proactive exploit detection by applying the mathematics and theory of bioinformatics. This approach is based on biomolecules such as genes and proteins being analogous to text strings that describe many aspects of the cyber universe. We aim to predict potential vulnerabilities in information technology or energy infrastructures, detect and remediate malware, and enable resilient, self defending networks. ◆

Many cyber security challenges result from a combination of scale and complexity. For example, understanding the intent of network transactions in the context of anomaly detection within the DOE complex requires analysis of an enormous, ever growing body of digital information to identify increasingly sophisticated attempts at infiltration and exploitation in an environment where the vast majority of transactions are benign. One limitation of these rule-based detection schemes is that we must first know what to look for, which is a challenge in the face of constantly evolving exploit methodologies.

This project is directed at developing capabilities to enable the construction of a collection of solutions to challenges in cyber and network security. The primary approach is to train computational systems to recognize patterns of interest in string based information (such as network transactions or legacy source code) using biological theory to capture the inexact and evolving relationships between text strings associated with digital information and use machine learning principles to extract patterns without a priori knowledge of those patterns. Success would have significant operational impact by enabling pattern based, data driven identification schemes grounded in a theoretical framework to augment the current rule-based approaches to cyber security. The intent is to develop algorithmic and computational infrastructure needed to deploy this concept rapidly into new problem spaces of cyber security.



Learning abstract patterns that correlate to various cyber events gives us the potential to recognize previously unseen events, whereas rule based systems rely on matching some feature of a known exploit.

In FY 2009, we accomplished the following:

Implementation of Parallel Support Vector Machines. Threaded approaches to support vector machine training were developed for both sparse and dense data representations. Threaded training shares the computational cost of creating an essential but extremely large data structure (kernel matrix) across many compute cores. We achieved near ideal scaling for matrix generation for up to eight threads, extracting as much efficiency from our compute hardware as possible. Improvements were also made to the serial algorithm at the heart of support vector machine training to improve significantly overall time to solution over competing implementations. These serial and threaded improvements will be the basis of a manuscript for submission.

Developing Letterization and Vectorization Strategies. Software for general purpose ingestion of raw data to a form amenable to bioinformatics analysis has been designed and implemented. This software is used to convert data from several sources (e.g., software binaries, network transaction log files) to a protein representation. In each case, the process of this ingestion is guided by the intent to condense as much of the data as possible into categorical event types (to keep the alphabet of our representation to a small number of characters) while preserving the functional essence of the text strings. This balance between specificity and generality is at the root of optimizing the letterization strategy for a given application and is intended to be an iterative process. For a single data type, one can ask many different questions that each would require a different letterization strategy to encode.

Once converted, the data to this representation have been analyzed using preliminary sequence analysis calculations to look for the presence of conserved character sequences (motifs) indicating related behavior. Motifs would form the basis of predictive signatures to look for in follow-on applications of this method for use in operational settings.

Managing Complexity of High-Volume Predictive and Adaptive Network Operations

Zhenyu Huang, Pak Chung Wong

◆ This project aims to develop algorithms and methods to manage the complexity of operations in critical infrastructures such as electric power grids, gas pipeline systems, telecommunication systems, and aviation networks. The outcomes are expected to provide real-time decision support to network operators to ensure safe and reliable critical infrastructures. ◆

Critical infrastructures play an important role in societies. Their failures, such as power grid blackouts, lead to significant disruption of peoples' lives, industry, and commercial activities and result in massive economic losses. Operation of these networks is a challenging task as they all have complex structures, wide geographical coverage, intricate data/information technology systems, and highly dynamic nonlinear behaviors with numerous internal configurations and external factors including physical attacks, cyber threats, human errors, and natural disasters. None of the operations is fully automated; human-in-the-loop operation is critical. There may be thousands of possible configurations that operators need to examine in near real-time during an emergency to choose the best option and operate the network effectively. In today's practice, networks are largely based on operator experience with limited real-time decision support, resulting in inadequate management of complex predictions and inability to anticipate, recognize, and respond to situations caused by human errors, natural disasters, and cyber attacks.

This project aims to establish a decision support system to manage complex predictions and help operators predict potential network failures and adapt the networks to adverse situations. The resultant decision support system will enable continuous monitoring of network performance, turn large amounts of data into actionable information, and maintain the integrity of the infrastructure.

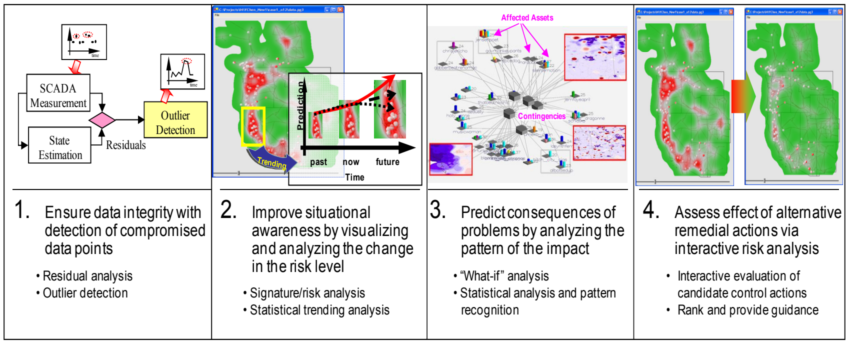
During FY 2008, we successfully developed methods for network risk analysis and visualization, graph trending analysis, and configuration clustering. In FY 2009, we progressed with a real-time decision support system in situational awareness software prototyping, data integrity assessment, and multiple predictions for future network operation. Some results were reported in a conference paper, and another was submitted to the *Journal of Energy Therapy*. One more paper on probability analysis is being prepared for the IEEE PES Transmission and Distribution Conference 2010.

The situational awareness prototype was also successfully evaluated by certified power grid operators in the visualization experiment. Operators expressed interest and overwhelmingly concluded that this new tool enabled them to recognize problems more quickly and respond to emergencies faster.

For data integrity assessment, we developed a residual analysis to detect statistical pattern change in measurement data. Any deviations from normal patterns would indicate compromised data due to either equipment malfunction or cyber manipulation. The residual analysis approach is implemented using BACON algorithm. Demonstrated by power grid examples, this implementation is more efficient and accurate than the traditional 3-σ method in detecting statistical outliers.

We also began to explore an approach that combines probability analysis and approximation expansion to perform a probabilistic risk assessment that predicts multiple possible futures for network operation. Probability density functions (PDFs) and cumulative density functions of network operation parameters are calculated in a four-phased approach: calculate PDFs of network operation parameters, divide PDFs curves into segments, calculate the approximate overall PDF of the system, and map the overall PDF to a risk index of a region or the whole system. One advantage is that it does not need time-consuming Monte Carlo simulations to obtain the PDFs; it is a fast approximation approach.

In FY 2010, we will continue efforts on refining and integrating the developed technologies. The goal is to develop an interactive evaluation of remedial actions on an integrated platform validated and verified with real scenarios such as power grid models and data. An integrated prototype tool will be developed to demonstrate the functionality of the decision support system. All tasks will continue to information and infrastructure security and reliability.



The decision support system consists of four basic elements: assess data integrity, recognize imminent problems, assess consequences of problems, and evaluate remedial actions.

MeDICI – Middleware for Data Intensive Computing

Ian Gorton, Adam S. Wynne, Justin P. Almquist, Jack Chatterton

◆ Creating advanced scientific simulations and intelligence analysis applications that must process large data sets is a difficult, time-consuming process. By reducing the complexity of application construction, this project is designing software solutions that will make application construction significantly easier and increase our capacity for scientific and threat discovery. ◆

Advanced scientific simulations and analytical applications typically require integrating multiple independently developed software modules into a single processing pipeline. This is a challenging task because the software modules were not originally designed to interoperate. Consequently, application designers must resort to custom, often one-time and prosaic, solutions to coordinate the execution of these modules and ensure they execute correctly and exchange data efficiently.

In FY 2007, we created the MeDICi integration framework (MIF) designed to make integrating software modules easier. MIF provides a consistent programming model and supporting software services that significantly lower the barriers to rapid interoperability and help automatically enable the efficient execution of the application pipeline. Importantly, this integration problem exists in all areas of science and intelligence analysis; therefore, if successfully designed and adopted, a cross-cutting general solution like MIF has the potential to have a broad, beneficial impact.

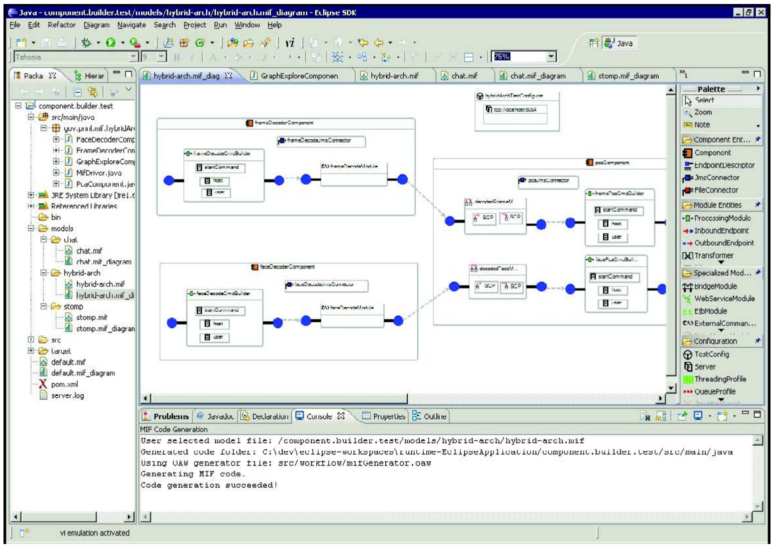
During FY 2008, we extended the core capabilities of the platform and validated its performance using a series of throughput and scalability benchmarks. We also created the MIF component builder tool that allows programmers to create applications graphically. MIF components are represented by icons in the component builder that can be configured by setting properties and connected to form application pipelines. When a design is completed graphically, MIF Java code to execute the application is automatically generated. At this point, our MeDICi wiki was able to provide detailed documentation and programming guides for application developers.

For FY 2009, we refined the MIF application programming interface (API) based on our experiences and that of users applying the technology. The API was ported to a new version of the underlying software infrastructure, providing immediate performance improvements and features such as deploying new components in an executing MIF application without restarting. We built a prototype extension to MIF for adaptive applications and performed an initial validation of this approach in a proteomics application.

We also worked extensively to design an efficient, usable interface to existing scientific workflow engines such as MeDICi Workflow and Kepler. Taking an atmospheric sciences application as a driver, we created an MIF catalog that enabled users to select existing MIF components in a workflow design tool and subsequently deployed a workflow built on an underlying collection of MIF components. We validated this makeup with application designers by implementing an existing complex application and demonstrating MIF benefits. This work led to two papers in highly competitive refereed conferences.

We continued to work with application designers to deploy the MIF platform and tools in several applications within PNNL and externally with collaborating institutions. Currently, MIF is used as an underlying software technology in several bioinformatics applications, cyber security analysis, and homeland security and is providing intelligent control of scientific instruments. Each of these application domains has distinctly different functional requirements, but the MIF technology is providing significant value to application designers in these projects. This provides considerable experience-based evidence that our approach is valid and that MIF technology is appropriate for use on diverse PNNL-developed applications.

This software is open source for use by the scientific and academic community. The web site contains extensive documentation, examples, and detailed instructions for installing the software.



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User selected model file: /component.builder.test/models/hybrid-arch/hybrid-arch.mif
Generated code folder: C:\dev\eclipse-workspaces\runtime-EclipseApplication/component.builder.test/src/main/java
Using OAW generator file: src/workflow/mifGenerator.oaw
Generating MIF code.
Code generation succeeded!
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The MeDICi integration framework (MIF) component builder.

Modeling of Microbial Communities in Soil Aggregates

Lee Ann McCue, Haluk Resat

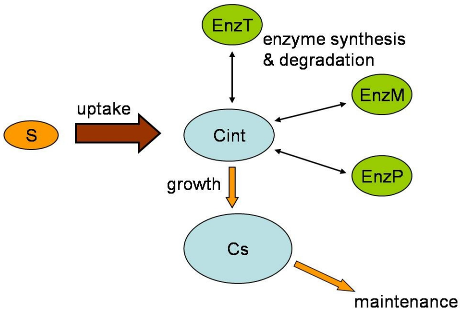
◆ To combat greenhouse gases, we need to enhance our understanding of the microbial communities to improve carbon sequestration in the soil. These ecosystems are extremely complicated and require sophisticated, realistic models of their activity and dynamics. ◆

Advances in mapping natural microbial flora and their activities make it possible to develop realistic models for the ecology of ecosystems. Soils are highly complex systems in terms of composition, dynamics, and heterogeneity. Approximately 1 g of soil contains about 10^9 bacteria and up to 1 km of fungal hyphae with diversity among microbes. Modern sequencing technology has enabled rapid, accurate mapping of environmental sample contents, providing species composition data needed for model development. Simulation software also enables building individual models of microbial ecosystems. Modeling a complex, dynamic system such as soil is challenging but vital to enhance carbon sequestration and combat rising levels of greenhouse gases. This project will develop technologies to analyze soil microbial communities to understand the metabolic capabilities and build three-dimensional agent-based community models. Computational techniques will be developed to analyze metagenome sequence data to infer microbial community composition and advance data analysis methods to improve peptide identification from complex microbial communities. Techniques and analysis of available data will be used to determine variation in community structure and activity within and between soil aggregates.

We analyzed data from two types of DNA sequencing technologies to map species in a microbial community. Both technologies targeted sequencing of phylogenetically informative ribosomal RNA encoding genes. Bar coded primers were used for soil communities, and Sanger sequencing for river communities. In FY 2008, we expanded our set of Perl scripts that process Sanger sequencing data to assemble full length ribosomal RNA gene sequences from multiple runs.

Because proteins are catalytically active components of cells, we extended data analysis efforts to proteomics to enable direct study of proteins present in an environmental sample such as soil. We tested the robustness of a model that predicts the peptides observable by mass spectrometry. We found that although the model has a defined microbial protein sample, it is robust to protein source, with strong predictive power for diverse samples. This demonstrates that incorporation of the model into proteomics data analysis could improve our ability to identify peptides and proteins in complex environmental samples.

Building on recent advances in bacterial ecosystems, we developed a model for energy and resource generation and utilization in microbial environments representative of soil microbial communities that incorporates the three-dimensional nature of soil. Our modeling and simulation approach allows for the coupling of cell dynamics to their internal kinetics in a single unified model, where each cell is described individually and its physiological response depends on its local environment. This approach explicitly takes spatial heterogeneities into account.



The biochemical reactions represented in our network models. Extra-cellular substrates (S) are taken up by the cell, allowing enzymes (EnzT, EnzM, EnzP) to act on the intracellular pool of carbon (C_{int}) and lead to sequestration of carbon (C_s).

Our simulation platform allows the use of kinetic models to describe the metabolic properties of cells through mechanistic biochemical reaction network models. In our model, cells uptake the external substrates to form an intermediate carbon pool C_{int} used to synthesize regulatory enzymes and for growth. Transport enzymes facilitate the substrate uptake and C_{int} levels are regulated by autocatalytic enzymes, which control expression level of an extracellular enzyme synthesized and released by cells to degrade polymeric carbon to its simpler substrate forms. This process makes the environmental carbon available for cellular uptake, and another facilitates cell maintenance related processes that can depend on the growth state of the cell.

As time is propagated simultaneously, cellular dynamics and decision making rules can depend on the internal state and the surrounding environment with better accuracy. Cellular energy production/consumption, substrate utilization, and product generation processes can be described at any desired level of detail in kinetic models for the internal dynamics of cells. Thus, there is no limit to treating microbial ecosystems in terms of energy and metabolite generation/consumption; the user can define energy and metabolite related networks at the detail level. Our platform can include three-dimensional taxis properties of microbes in models of individual cells or any size colony.

Modular Network Modeling of Inflammatory Pathways

Katrina M. Waters, Harish Shankaran, Jason E. McDermott, Brian D. Thrall

◆ This project will use particle induced inflammation in macrophage and epithelial cells as a model system to compare standard gene regulatory networks to pathway based modular networks. We will demonstrate new bioinformatic capabilities for mechanistic modeling of cell response pathways that describe paracrine interactions of multicellular systems from integrated microarray and proteomic data. ◆

A fundamental premise of systems biology is that complex biological system behavior can be predicted through integration of high dimension data and computational modeling. Developing mechanistic (predictive) models of cell signaling networks in mammalian systems is a challenge due to system complexity, practical limitations in systems level data, and computational limitations for dealing with the data. To address these issues, we will develop modular network modeling that captures the complexity of mammalian signaling networks that are computationally scalable and generalizable to new biological problems. This approach will combine methods for statistical ontology (functional) enrichment and network inference methods to reconstruct cell response networks from integrated genomic and proteomic data. Unlike gene regulatory networks, our approach will define cell processes (biological pathways) as nodes of a response network.

Particle induced inflammation will be used as a model system to compare standard gene regulatory networks to pathway based modular networks from microarray and proteomic data in macrophage and epithelial cells. Taking advantage of the comprehensive nature of genomic and proteomic data, define dynamic cell response networks will be defined using a modular representation of the data at the pathway level and a network model generated of macrophage epithelial cell interactions during the inflammatory response to silica particle exposure. Pathway "sentinels" will be identified to validate the structure of the network topologies, and molecular knock down experiments will be performed to evaluate the predictive nature of the model. The ultimate goal is to develop a strategy to create mechanistic models of cell response from integrated, high throughput data using a combination of experimental and computational approaches.

Our project work focused on developing bioinformatic methods for modular network modeling using macrophage response data to particle exposure and characterizing the macrophage/epithelial cell co culture system. The macrophage time course microarray data was collected through leveraged project work. A primary objective in FY 2008 was to determine a method for identifying functional modules from global response data (microarray/proteomics). Gene set enrichment analysis is a statistical approach that determines if genes within a particular biological function (cell process) are over represented in a dataset. We used the Fatigo enrichment tool on our microarray datasets to determine how macrophage response pathways change as functions of particle dose and time. Comparing cellular process enrichment scores across time points, we identified a process cluster associated with defense and inflammatory responses that appear temporally linked to the dose dependent apoptosis. We also identified cell process clusters that suggest regulatory mechanisms for dose dependent transitions from adaptive to toxic responses.

In FY 2009, our modeling efforts focused on generating gene regulatory networks and computational methods for isolating functional modules within network structures. We discovered that not all genes within cell process categories have the same temporal or dose dependent expression profile; therefore, we developed a cluste approach to determine the appropriate number of subprocess modules to capture multiple profiles within a each category. We determined sentinels for these subprocesses as the gene that had maximal fold change representative of the subprocess profile. Correlation based network analysis calculated bottleneck nodes within data, since these often do not share the expression profiles of the functional module they regulate. Combining methods enabled the identification of modules, sentinels, and bottlenecks for use in dynamic Bayesian network modeling. Our macrophage/ epithelial cell co culture experiments focused on validating computational findings of regulatory bottlenecks by demonstrating that pharmacological inhibitors completely abrogated the inflammatory response of macrophage cells to nanoparticle exposure. We demonstrated that genetic knockdown of secretion blocked subsequent induction of apoptosis in macrophage cells. In response to reviewer comments, we further validated that the marker genes we identified from the macrophage cell line to be responsive to nanoparticle exposure in alveolar macrophage cells.

The final phase of wet lab studies focused on the reverse exposure system: treating epithelial cells in the bottom chamber with silica particles and looking for inflammatory responses in both macrophage and epithelial cell layers. We performed a microarray analysis of epithelial cell response to particle exposure to identify marker genes for time and dose dependent expression studies. Using these data, we ran quantitative studies of marker gene regulation over dose and time for two different particle sizes in order to capture a conserved mode of action for our network modeling. Combined with our macrophage data, we have both halves of our paracrine system characterized to start assembling our cell interaction network model.

Multiscale Models for Microbial Communities

Haluk Resat

◆ This project aims to develop models and simulation methods for studying the dynamical properties of microbial communities. In particular, models and simulation algorithms will be developed to study the carbon and energy metabolism properties of microbial communities in engineered microfluidic growth environments and in heterogeneous soil systems. ◆

Soil is a highly complex heterogeneous system, both in terms of its inhabitant microorganisms and its spatial properties. Soil structure can be thought of as a dynamic hierarchy of aggregates of different sizes that contain microbial cells with different metabolic properties. Such variations in local environmental conditions are expected to lead to a widely varying distribution in the dynamics of the microbial cells. In terms of mathematical modeling, this translates to having a heterogeneous system in which participating objects have different classes of dynamical properties: some would show strong individual characteristics that require explicit treatment, some would be part of multicellular assemblies that mimic large well mixed systems, and some would be exposed to in between conditions.

In short, the kinetic properties of microbial organisms are dependent on the physical, chemical, and biological composition of the systems in which they are a part. Therefore, investigation at the whole community level is required for a more comprehensive understanding of microbial systems. The main aim of this project is to develop novel mathematical models that incorporate the possible effects of heterogeneous three-dimensional structure, functional biodiversity of the microbial population, and geochemical processes into a unified model. This will improve our understanding of the role of interaction of bacterial and fungal metabolism in the transformation and sequestration of soil carbon, and contribute to predicting the impact of microbial community based management practices in controlling and regulating carbon flow in soils.

Variations in the local conditions can impose different environmental cues on microbial cells and this can lead to widely distributed physiological responses in a population of cells. This is particularly the case for microbial communities in heterogeneous systems where the differences in the local environmental conditions can have a large effect on the cellular dynamics and physiology. Building on recent advances in the modeling of bacterial ecosystems, we are constructing a hybrid, multiscale mathematical model for resource generation and utilization in environments that are representative of the microbial communities in natural soil aggregates. As sequestration of terrestrial carbon via microbial and chemical reactions in soil can offset some of fossil fuel carbon emissions to lower greenhouse gas release, better understanding of the transformation of carbon in soil systems and the flux and residence times of different carbon forms will enable greater understanding of the terrestrial carbon sequestration processes.

Challenging the existing paradigms. In FY 2009, our modeling and simulation approach allowed for the coupling of the dynamics of the cells to their internal kinetics in a single, unified model while retaining the strengths of the earlier efforts. Unlike others, our simulation platform makes it possible to use agent-based formalism without a time scale separation assumption. Our platform also allows for the use of kinetic models to describe the metabolic properties of the cells through mechanistic biochemical reaction network models, where rules can be imposed at the individual cell scale according to their physiological states.

Model overview. Also, in FY 2009, we investigated the role of heterogeneity on the dynamics of microbial communities is one of the major goals of this project. Such heterogeneity can arise both in terms of organism composition and spatial distributions. Arguably, the most important aspect of composition heterogeneity is how different species coexist and affect each other's behavior. Thus, instead of trying to construct accurate network models for a particular organism, our model building efforts emphasize interdependent relationships between observed species in terms of their shared energy and metabolite utilization dynamics.

Hybrid representation. Our approach makes use of a hybrid construction and combines lattice and individual based representations. In FY 2009, we constructed a rectangular grid lattice to identify the solid filled and porous parts of an aggregate. Each grid element has a unit length of approximately 5 micron, the size resolution in our model.

After building the models for carbon and energy generation and using them for simple microbial communities residing in heterogeneous soil structures, our plan during FY 2010 includes analyzing the microbial dynamics patterns as a function of soil porosity and aggregate sizes. Sensitivity analysis to the kinetic rate parameters of the model will also be pursued. We will then adapt the simple community model to microfluidics setups to simulate the growth dynamics in engineered systems, and these simulations will aid the design of the planned experiments.

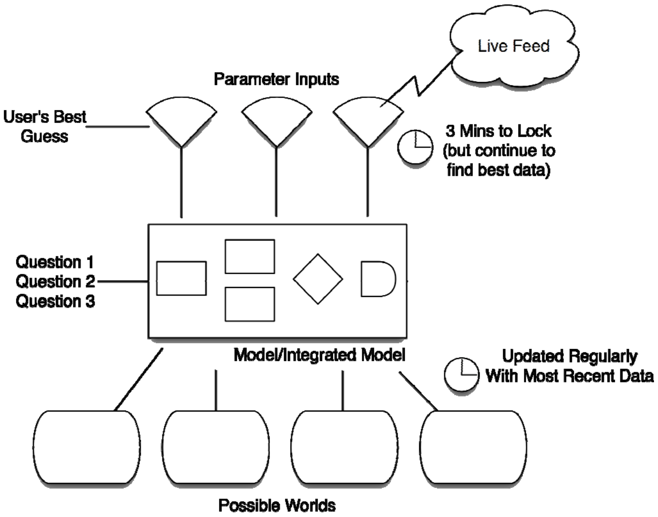
Precision Information Fusion Environments

Andrew J. Cowell, William A. Pike, Lyndsey R. Franklin, Sam Hashemi, Brian S. Minsk,
Jonathan L. Barr

◆ This research will design and implement technologies to support the next-generation precision fusion centers that tackle issues relating to timely information sharing, access and alignment, and arrangement of information. If successful, our created prototype environment has the potential to become an integral part of threat analysis, emergency planning, training, response, recovery, and decision-making across multiple domains. ◆

Information fusion provides a means of bringing together information from distributed sources and models for the purpose of integration, analysis, decision-making, and dissemination. While information fusion is a powerful concept in theory, information access policies and data incompatibilities reduce the efficiency of such processes. Our project aims to create a collaborative computing environment that aids users in their information discovery task with integrated information delivered precisely to fulfill their current needs, while enabling effective interaction and collaboration with both local and remote colleagues.

Our focus in FY 2009 was on the tactical response to chemical, biological, radiological, or nuclear terrorist events, and the development of an efficient computer architecture that can automatically gather inputs required by models and forecast potential possible worlds. These worlds are pruned as new data, and user-driven actions make them less likely, continually providing a view on potential future states.



An integrated model and simulation to provide a tactical capability to EOC staff designed in the over architecture for this environment.

Responding to emergency situations is an unbelievably challenging task. The Emergency Operations Center that typically sits silent becomes a rush of people wearing colorful jackets, with acronyms on the back defining their role. Data are either overwhelming or in short supply, and defined protocols useful in training become vulnerable in the stark reality of a real emergency. People start to rely on historical situations, personal experience, and best guesses to get them through, unsure if their actions will help or hinder unfolding event. During FY 2009, we conducted research in three major areas. The first was selecting a domain to apply precision information fusion environment concepts and then understanding that domain (emergency management) in enough depth that we could create a demonstration of capability. This task was done via literature review as well as through running ethnographic studies with personnel from the Benton County Emergency Management division. These studies involved observing what individuals would do in a real emergency setting. This allowed us to identify cognitive task models for each role that can inform the design of the precision fusion environment.

Based on the task models, we developed a prototype interface as a sandbox to compare and contrast the utility and importance of the different aspects of precision information fusion environments. These aspects included visualization, automated data identification and delivery, architectures, and geospatial interfaces. Finally, we designed the overarching architecture for the environment. System complexity can be an issue in stressful decision making. For this reason, the user interface for the environment (to be developed in FY 2010) shall be designed to be simple and efficient, offering from a small number of dedicated options. Based on the question selected, models within the architecture are selected and connected dynamically. As time is a factor, the system will try to align data inputs for the models automatically. If sufficient matches are not found, historical data or best guess will be used. After a set period, the environment takes the best data and produces a set of "possible worlds" to describe worst to best case. The environment will attempt to find more accurate data inputs and refine each scenario. Occasionally, scenarios will be pruned as it becomes clear that scenario is highly unlikely. To operationalize this scenario in FY 2009, we spent some effort finding a suitable set of models and identifying a suitable middleware architecture in MeDICi. This work has produced two draft papers, one that highlights the physical and cognitive challenges in emergency management and another that reviews the state of modeling and simulation in this domain.

Predictive Adaptive Classification Model for Analysis and Notification: Internal Threat (PACMAN-IT)

Frank L. Greitzer, Patrick R. Paulson, Thomas Edgar, Lars J. Kangas, Lyndsey R. Franklin,
Ryan E. Hohimer, Thomas E. Carroll, Christine F. Noonan, Angela C. Dalton

◆ This research aims to develop a predictive classification-based reasoning system to detect, forecast, and deter malicious insider activity. The general reasoning system applies to a range of predictive analysis domains that address critical national security needs. ◆

Espionage and sabotage involving computer networks are among the most pressing cyber security challenges that threaten government and private sector information infrastructures. No single technique of intrusion detection or threat assessment gives a complete picture of the insider threat problem. Current practice in insider threat detection tends to be reactive, as it focuses on detecting malicious acts after they occur with the aim of identifying and disciplining the perpetrator. Recent studies have identified a prominent role of psychosocial factors. This information is distinctive, as no current system integrates cyber and psychosocial data into a predictive framework. Thus, defining possible precursors in terms of behavioral observable cyber and psychosocial indicators is one of the major challenges in developing a predictive methodology.

During FY 2007, we described the initial framework and predictive modeling concept, PACMAN:IT, for insider threat prediction and mitigation. We defined and implemented select predictive algorithms, addressing the threat indicators preceding the exploit. Recognizing the imperative to address both human and non-human elements that comprise the insider threat, we defined possible precursors in terms of behavioral, observable cyber indicators. Additionally, we proposed basic concepts for PACMAN:IT, specifying initial algorithms (pseudo-code) for classification and implementing prototypes of two components: the dynamic Bayesian, a network to infer whether an employee was logged in and working at his/her workstation, and a component that focused on integrating inferred psychological or psychosocial indicators with cyber data to predict possible exploits. Further, we developed a web services architecture and object-oriented design to provide an extensible, flexible, adaptive, and modular framework for the various components within the predictive modeling framework.

In FY 2008, we focused on project implementation. A service-oriented architecture and object-oriented design provided an extensible, flexible, adaptive, and modular framework within which to implement the model. The main predictive component was the Reasoner, which uses description logic formulas to process observations of class membership and infer indicators. Behaviors were modeled as finite-state machines. In combination with previously inferred indicators and behaviors, the Reasoner assessed current indicators in order to determine the likelihood of behaviors that represented a threat. Temporal relationships were expressed as finite automata, and events moved the automata from one state to another. Additional accomplishments during this fiscal year included development of a user interface that demonstrated operation of the model and a component to simulate data that may be used to evaluate the model's performance.

A preliminary evaluation study yielded promising, statistically significant results, reflecting the ability of the model to detect suspicious (precursor) activities. As part of our research on the psychosocial foundations and details of the model, we addressed organizational security, privacy, human subjects, and potential legal issues surrounding the monitoring of such data and documented our findings and recommendations in an internal technical report.

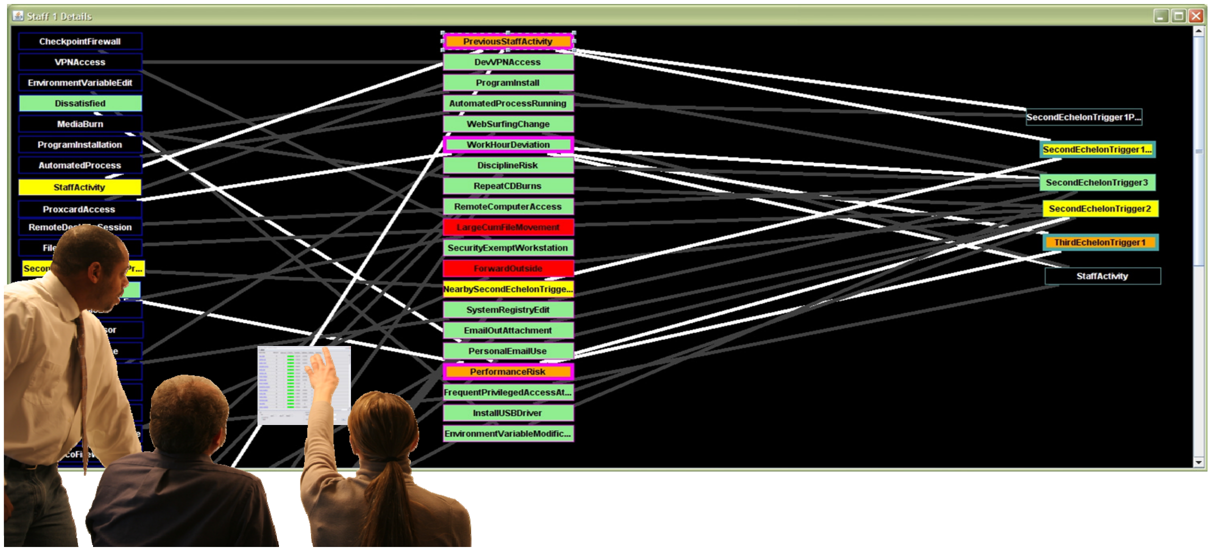
Going into FY 2009, we continued to refine the modeling and design concepts, further informed the psychosocial model parameters, implemented the theoretical model-based approach to prediction using a finite state automata and Bayesian inference framework, and conducted several tests of the prototype. We prepared a technical report that documented research findings, conducted and published a panel session paper at the 2008 Annual Computer Security Applications Conference, submitted a paper for publication, and wrote several invited book chapters.

Our research has developed a framework for and implemented a predictive model-based system (Psyber Sleuth™) that takes account of psychosocial and cyber indicators of potential insider threats. At the foundation of Psyber Sleuth is a knowledge base of cyber and social indicators that informs all other components of the model. Components of the model perform functions of data collection, data fusion, analysis, and decision making. The analysis progresses from data to observations to indicators to behaviors: data are classified into observations, which in turn are examined to infer indicators and are thus evaluated to infer possible malicious exploits (behaviors). This is an iterative process in which increased suspicion leads to more analysis, more data collection, and increased focus on some indicators. The main predictive component was once again the Reasoner, which additionally identified patterns of behavior that were of interest. A dynamic Bayesian network stored the current position or status in the finite state machine, where the system analyzed both cyber and psychosocial data. A psychosocial model component implemented as a Bayesian network was developed based on knowledge engineering interviews with human resource experts. The psychosocial model used 12 behavioral indicators to generate a risk level estimate. We refined both the Reasoner and the psychosocial model through analysis and vetting of their constituent rules or factors.

Additionally during FY 2009, we implemented major enhancements to the Psyber Sleuth user interface, including visualizations that expose the operation of the model and support joint human-computer decision making. The system demonstration is most effective when viewed on the large multi-pixel, multi-monitor system in the cyber analytics laboratory as depicted below, but it also runs on a single-display system.

We also conducted major evaluation studies to test the Psyber Sleuth cyber and psychosocial components. First, we performed a test of the Reasoner against data provided by the Institute of Electrical and Electronics Engineers Symposium on Visual Analytics Science and Technology demonstrated that the system successfully identified all of the malicious events and correctly identified the perpetrator out of a simulated population of 60 employees. Compared to human cyber analysts and given the same data who were unable to make any progress after two hours of examination, the Psyber Sleuth system yielded a solution in one hour of real time, demonstrating an obvious positive impact in enhancing analysis. Further, we conducted a verification test of the psychosocial model by obtaining ratings from 10 expert human resource and management personnel on 24 scenarios. The number of observed psychosocial indicators varied from 1 to 5. Inter-rater agreement on the 24 scenarios was high: pairwise mean Pearson correlation = 0.74, variance = 0.009; intraclass correlation coefficient = 0.65, where 1.0 = perfect agreement, and inter-rater reliability coefficient with Spearman-Brown correction = 0.95. The psychosocial Bayesian model yielded a good fit to the aggregated expert ratings ($R^2 = 0.60$).

This project received national recognition accolades, including an invitation from the National Academy of Sciences to participate in workshop on usable security as a provocateur. Publications have included addressing organizational security, privacy, human subjects, and potential legal issues surrounding the monitoring of employee data as well as authoring three chapters in two different books on insider threat and information assurance. Further studies include focusing on attack pattern recognition for smart grid and an ongoing maritime drug interdiction project using the Reasoner to classify and recognize possible suspicious activities.



Advanced visualization provides insight on possible attack patterns and exploits of individual employees. The display enables the analyst to explore the reasoning and evidence underlying the system's output.

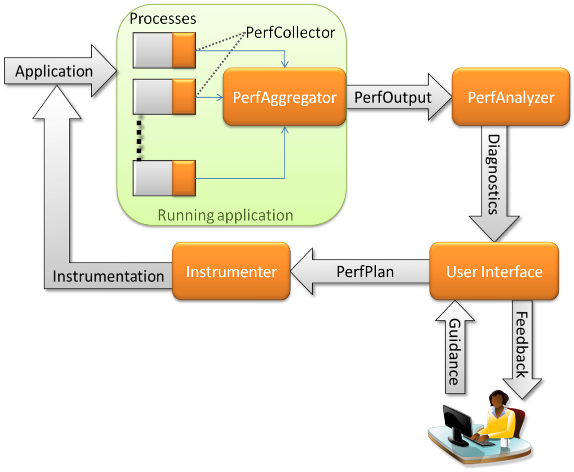
Scalable Performance Diagnostics and Feedback for Massively Parallel Computers

Sriram Krishnamoorthy

◆ Effective utilization of current and future supercomputers for science requires application performance at scale. This project aims to develop capabilities to identify performance bottlenecks quickly and inhibitors of scalability, focusing on inter process communication. ◆

While characterizing communication behavior has been widely studied, a fundamental limitation of existing tools and approaches has been their limited usability in parallel programs running on large numbers of processors and their inflexibility in the information collected. Among the issues encountered are overhead to the profiled running program, managing the sheer size of the profiles generated, and providing insightful feedback to users rather than flooding them with raw data. Improvements in single processor performance through an increase in clock speed have been severely limited by the problems of power consumption and dissipation. High end computers used for large-scale scientific calculations employ increasingly larger processor counts to achieve greater performance. The future exascale computers can be expected to contain up to millions of processors, with their complex interaction further complicating application scalability.

We shall address these issues in the context of the Global Arrays programming suite, the model used to develop key applications at PNNL. This project targets the development of suite capabilities to identify performance bottlenecks and inhibitors of scalability. We will increase understanding of the application characteristics through profiling to provide insights into their performance on future parallel systems. Our approach aims to allow better tuning of application performance, which will reduce time spent in tuning, allowing users to focus on newer functionality. Scientists will obtain an understanding of the performance characteristics of their application, enabling a more accurate estimate of the impact of their design choices on overall application performance before implementation is complete and a large enough system is available to evaluate the implementation. Applications can thus be developed that will be ready to exploit the next generation parallel systems when they become available.



Performance optimization process.

The performance and analysis tuning process we envision is shown in the graphic. The application developer can provide useful domain specific information to simplify performance collection and analysis. Additionally, the user can decide the level of detail and the components measured to tailor the data collected to meet the needs at hand. Such information would be used to decide the appropriate instrumentation in the program, which is then executed. The performance information from the different processes is collected and aggregated to derive a composite performance output. This output can be directly viewed by the user or run through various analyses for common performance bottlenecks. These steps can be repeated by the user to further tune the application.

A scalable communication trace compression technique has been developed. The approach extends a popular text compression algorithm to locate and compress identical patterns of communication across processes participating in the parallel execution. Evaluation using a standard benchmark suite demonstrates improved compression achieved over existing techniques. We are currently developing algorithms to identify similar, rather than just identical patterns that would further improve the compression achieved. The results obtained from the combined algorithm will be submitted for publication.

A preliminary version of a profile collection framework has been developed. The profile consists of ARMCI communication information stored in a relational database format. The framework will allow development of a performance data repository that can be queried for performance analysis and feedback. A demonstration of the framework and associated tools was given to some members of the subsurface modeling project. We are involved in providing an improved version that incorporates their feedback to the scientists for their usage.

In FY 2010, we will provide performance profiling tool to the application scientists. We plan to develop summarization techniques for our trace collection approach. Further improves its scalability. We will also investigate integration of these approaches into existing tools for broader applicability.

Scientific Metadata Services (SMS) Architecture

Eric G. Stephan

◆ To protect the investment of vast amounts of raw scientific evidence, we need to provide software services capable of making data more accessible. Accessibility is made by identifying software services that help users analyze their data through the use of provenance, metadata, and a search engine capable of working with large-scale scientific data. ◆

Systems science is the interdisciplinary study of the complex behavior of physical phenomena, such as living organisms or climate studies that rely on the analysis of large-scale data produced from scientific instrumentation, theoretical computations, simulations, and complex analyses. The analytical input decks, intermediate results, and data products are structured in a variety of formats and stored physically in archives, file systems, and grids. To address key scientific challenges, today's scientists are faced with manually accessing, distilling, and synthesizing data sources to products in the form of visualizations, diagrams, data spreadsheets, and summary reports. These products are used to help convey discoveries and insights to their respective communities. Finalizing these products, however, requires personal knowledge about the data, and it is time-consuming work to harvest, extract, and assemble the results. While this approach has served the scientific community suitably at the gigascale, it is inconceivable that data products grow in abundance and scale to the terascale and eventually exascale. To cope with these new scales, some scientists have resorted to developing hard wired software solutions to analyze the data. Over time, these sandbox solutions are often obscure and difficult to maintain because the software is written around a particular problem, so redundancy and overlapping code may result.

Our research goal is to identify common software services that will be used for analysis of high performance computational and experimental data. The SMS will be designed to scale through use of distributed software services, metadata repositories, ontologies, and harvesters. Research will be guided by partnering with the PNNL scientific community and external biological collaborators for feedback on the value of research projects' contributions. We aim to identify and design core software components required to advanced data analysis capabilities for systems science. Our design will be based on relevant real-world large-scale system science needs that involve experimental and computational data such as molecular dynamics, proteomics, computational biology, and bioinformatics.

In FY 2008, our research encompassed the study of scientific data, usage patterns, and data sources that tied directly to uses such as citation databases. We used this approach to identify software services because previous experience showed that simply relying on interviews failed to expose entire users' present needs, give a dynamic perspective of the users' ever changing needs, and identify adequately communities of users having similar needs. Our preliminary research showed that it is possible to establish living requirements by building knowledge repository from identified stores, mining required collection points to verify problems and solutions, identify new services and assess their impacts, and identify overlaps and interdependencies between differing domains.

In FY 2009, the project's primary achievement was retaining a data management key hire active in scientific data management research within the e-Science community. Additionally, a collaboration with the Stanford Linear Accelerator Center was initiated and a colloquium series established to exchange knowledge on the scientific challenges of each institution faced and data management solutions for large scale complex scientific data management. The goal is to ascertain the systems sciences challenges faced throughout the scientific community and the data management solutions being pursued.

Finally, the project developed a use case to help meet research objectives in large scale provenance management by forming a collaboration on scientific capture, management, and storage. A provenance use case was identified pertinent to atmospheric and global climate research involving provenance collected from remote sensor measurement models. These models were built by combining raw sensor data streams algorithmically providing a seamless profile weather conditions. What was most interesting about this use case was that provenance captured at the sample time step is significantly larger than the sample it is describing. This led to a multi tier provenance model specification, a publication, and an initial investigation on how graph analysis can be applied to detecting trends and anomalies in provenance data. It also led to research on how to collect provenance from existing resources such as crude log files created and used by developers of the measurement models.

Tactical Deployment and Management of Adaptive Agents

Glenn A. Fink, Jereme N. Haack, Wendy M. Maiden, Errin Fulp (Wake Forest University)

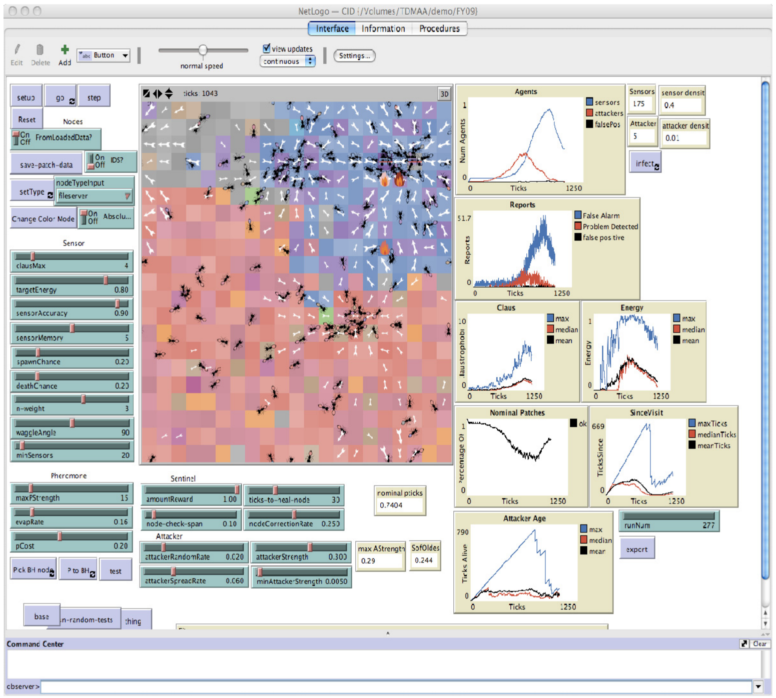
◆ This research aims to develop a framework for diverse organizations within a critical infrastructure to secure their cyber assets cooperatively. Tactical deployment and management of adaptive agents addresses critical needs of national security for resilient, self-defending networks to decrease time between attack onset and remediation. ◆

The tremendous speed of attackers on today's networks and machines has driven defenders to rely on automation to separate misuse attempts from legitimate use of cyber resources. The ultimate cyber defense objective for many is a completely autonomous system that defends computer resources in the background, allowing normal business to proceed unobstructed. Humans will always be responsible for the actions of their machines, so it is critically important that we be able to monitor and guide systems, particularly when they are used to protect safety-critical systems and infrastructures.

This project has defined a cooperative infrastructure defense framework that enables groups of interdependent enclaves to defend their cyber assets collaboratively via a society of humans and autonomous adaptive software agents. The enclaves in an infrastructure share common overarching operational goals and may share physical equipment, but they generally do not share policies or other process information. Examples of this type of infrastructure include the computers and networks supporting our national electric power grid, the distributed, heterogeneous computing collaboratories used in open science, or the computer equipment used to support partner countries in coalition warfare. We sought to discover ways that humans can exert supervisory influence on the system while retaining the rapid, adaptive response.

Tactical deployment and management of adaptive agents have adapted ideas from social insect behavior models for cyber defense in a digital environment and developed heuristic models to discover parameters that influence the behavior of these systems. We conducted sensitivity testing to determine the most influential parameters to overall long-term system behavior. We discovered two lever parameters that serve as goals for supervising the behavior of societies of agents: target activation level and target crowding level. By adjusting these parameters, human supervisors can change the behavior of all system-wide agents.

During FY 2007, we built four prototypes: two for the purpose of understanding the dynamical behavior of sensors and two to investigate alternative models of sensor behavior based on social insect communication (e.g., ants and bees). We produced a study of the behavior of the ant model that showed how the sensors can control invading attackers via emergent, self-organizing behavior that arises from simple rules. Our most important finding was the discovery of two factors that influence sensor population levels without external control. We published a paper on autonomic computing related to this work.



nodeTypeInput: fileserver
clausMax 4
targetEnergy 0.80
sensorAccuracy 0.90
sensorMemory 5
spawnChance 0.20
deathChance 0.20
n-weight 3
waggleAngle 90
minSensors 20
maxPStrength 15
evapRate 0.16
pCost 0.20
amountReward 1.00
ticks-to-heal-node 30
node-check-span 0.10
nodeCorrectionRate 0.250
attackerRandomRate 0.020
attackerStrength 0.300
attackerSpreadRate 0.060
minAttackerStrength 0.0050
nominal patches 0.7404
max AStrength 0.29
SofOldes 0.244
Sensors 175
sensor densit 0.4
Attacker 5
attacker densit 0.01
runNum 277

Tactical deployment and management of adaptive agents graphical user interface showing ant-colony behaviors, including pheromone following.

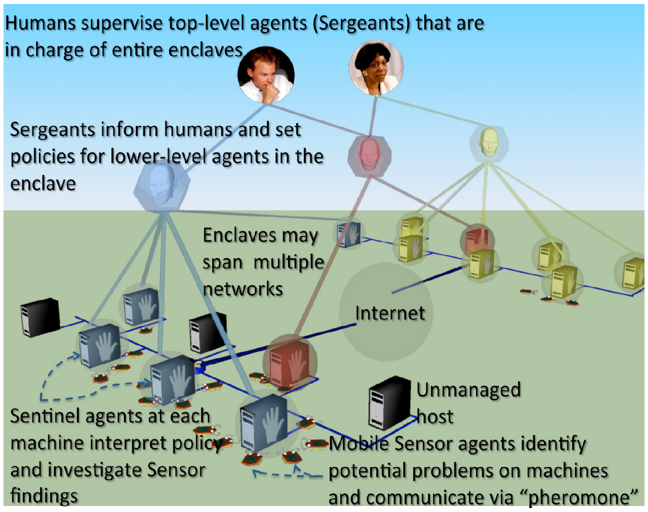
In FY 2008, we more carefully defined the full framework and each relationship within. We analyzed system failure modes and inherent weaknesses in our algorithms in an effort to understand ideal conditions and constraints for using this approach to cyber security and devised an initial approach for trust management to mitigate failure modes. In addition, we made progress in sensors' mobility and their ability to classify data. We updated the mobility simulation to use ant colony algorithms and three kinds of indicators (as opposed to the single indicator model used previously). We then created an algorithm to translate the discontinuous geography of cyber space into a discrete-continuous space suitable for ant algorithms.

While developing algorithms for the classifiers used by mobile sensors, we discovered a method of predicting hard disk failure with 80 percent accuracy within a 48-hour window. We completed preliminary automated analysis work using support vector machines to predict and detect these failures using syslog data from PNNL's 1100-node MPP2 cluster computer. This approach could use the same techniques to train classifiers to predict or detect events of cyber security interest.

Our project research in FY 2009 yielded the publication of seven papers (including one book chapter) as the products of our collaborations with Wake Forest University, Virginia Polytechnic Institute and State University, and Utah State University. We presented posters at the 2009 Workshop of the Analysis of System Logs and gave an invited talk on the mathematics of cyber security at the Society for Industrial and Applied Mathematics conference on computational science and engineering. Also this year, the tactical deployment and management of adaptive agents staff have presented our work at three international conferences. We plan further publications based on the work even after the close of the fiscal year.

In FY 2009, we concentrated on implementation of a cooperative infrastructure defense demonstration system based on a set of 64 virtual Linux machines. We isolated the testbed from other networks and released real Linux worms against the systems. The cooperative infrastructure defense agents had never seen these worms before, yet they detected them in a matter of minutes. We did not broach the topic of automated recovery of infected nodes, but this is an avenue for future work.

In cooperative infrastructure defense, humans and various types of software agents share the responsibilities of securing an infrastructure comprised of enclaves that belong to member organizations. The figure shows how one human can supervise a multi-enclave system with a few enclave-level agents, a host-level agent at each machine or group of similar machines, and a large swarm of simple mobile agents. Humans function as supervisors, who provide guidance to and receive feedback from one or more enclaves. They take action only when the lower-level agents encounter a problem that requires human involvement.



Cooperative infrastructure defense is a hierarchical framework of human supervisors, enclave-level rational agents, and swarming agents. A single human may supervise multiple enclaves via the agent hierarchy.

Enclave-level agents called sergeants are responsible for the security state of an entire enclave. Sergeants dialogue with humans to gain guidance for running the system according to business drivers and human security policies. Additionally, sergeants create and enforce executable policies for the entire enclave. Host-level agents called sentinels protect and configure a single host or a collection of similarly configured hosts such as a cluster or storage network. Sentinels interact with human supervisors only when they need clarification about how to classify ambiguous evidence from the swarm. Swarming agents called sensors roam from machine to machine within their enclave, searching for problems and reporting to the appropriate sentinel. Sensors are diverse; their classifiers are each uniquely derived from the set of known problem indicators. Sensors use stigmergic messages called digital pheromone to communicate.

Also during FY 2009, we investigated trust management more fully and discovered that existing trust frameworks were insufficient for swarming agent security systems. We then designed a new approach and published a paper on it. Trust management for existing mobile agent frameworks usually center around an e-commerce model. These agents require centralized coordination, have predefined itineraries, and seek to avoid malicious hosts. In contrast, our problem space requires agents to visit and repair compromised machines, to move abut in a random stagger, and to cooperate without centralized communication methods. Cooperative infrastructure defense mobile agents are lightweight and involve no actual mobile code; instead, they pass state from machine to machine within the enclave. Our new approach to trust management for cooperative infrastructure defense, moves trust maintenance responsibilities up to the sentinel level.

We expanded the disk failure prediction work to include predictions of failure for a wider variety of components. We implemented predictions using syslog and other data from the new Chinook supercomputer at PNNL and expanded a prior invention report on the approach. The objective is to predict and prevent events that would require human intervention. We believe that by sharing system control with a hierarchy of agents and using the truly adaptive capabilities of swarm intelligence, we can greatly enhance the security of our computational infrastructures and the societies that depend on them.

Ultrascalable Solvers for Subsurface Simulation

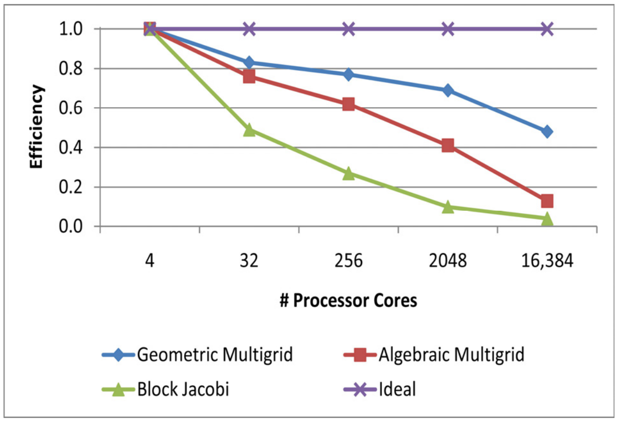
Glenn Hammond, Barry Lee

◆ As DOE invests in high-performance computing facilities and the development of scientific software to be employed at these facilities, it is important that the software make full and efficient use of the supercomputing hardware to maximize the resulting benefit to society. This project researches the development of enhanced solver algorithms that improve the efficiency of parallel subsurface groundwater flow and contaminant transport codes for investigating environmental remedial action alternatives and performance assessments. ◆

Subsurface flow and reactive transport codes play a vital role in accomplishing specific environmental stewardship objectives. These simulators enable scientists to predict the migration of contaminants in the earth's subsurface and evaluate the efficacy of proposed long-term waste repositories and site remediation alternatives long before technologies are deployed in the field. Built on mathematical equations that govern groundwater flow and contaminant transport in the subsurface, these codes utilize solvers to resolve equations. For years, solver algorithms have been effective at resolving these mathematical equations on desktop computers and small parallel computers. However, as supercomputers increase to extreme numbers of processors (e.g., peta- and exascale, termed extreme-scale computing), it is unclear how solvers will perform on advanced machines.

This project is developing ultrascalable solvers for massively parallel subsurface multiphase reactive flow and transport simulators. One weakness of existing parallel simulators is that solver performance tends to break down as problem size increases or the number of processors cores employed in parallel grows, resulting in often efficient use of computational resources. With computational science approaching exascale, solver scalability (or lack thereof) will become one of the primary bottlenecks in subsurface simulation. In our research, novel algorithms will be investigated for the scalable solution of nonlinear systems of partial differential equations governing subsurface multiphase flow and multicomponent reactive transport. Physics-based preconditioning and multilevel methods provide algorithms for ultrascalable parallel computation that will be investigated and implemented within PNNL's subsurface simulators (i.e., STOMP). This research will develop core applied mathematics capability at PNNL in numerical analysis and Newton-Krylov solvers.

In FY 2009, we have been developing improved solver algorithms that exhibit better efficiency than current techniques. The end goal is to incorporate these increasingly efficient solver algorithms within PNNL's eSTOMP simulator and employ them to resolve real-world flow and transport problems. To date, we have evaluated the performance of existing solver technology on large subsurface flow and transport problems composed of over 134 million unknowns on up to 16,384 processor cores. To provide a frame of reference, most existing subsurface simulators solve problems composed of 10,000 to 100,000 unknowns on one processor core. Therefore, we are assessing the performance of these algorithms at the extreme scale for subsurface simulation. Results of this research have demonstrated that the efficiency of existing solver technology degrades as the number of processor cores increases. This phenomenon is illustrated in the figure, where efficiency is plotted versus the number of processor cores employed for a nonlinear groundwater flow problem solved with several conventional solvers. Here, the ideal efficiency is one. Although not ideal, the multigrid algorithms perform better than the conventional block Jacobi. This superior performance was achieved by modifying and optimizing the multigrid algorithms for solving subsurface flow.



Efficiency of conventional solver algorithms for a fixed-size subsurface problem as the number of processor cores increases from 4 to 16384.

For FY 2010, we will focus our efforts on further improving the performance of these more scalable solvers by redesigning their algorithms to make them more compatible with the inter-processor communication fabrics of extreme-scale supercomputers. Further, we are studying the coupling of scientific processes in the subsurface simulator, with the goal of leveraging our knowledge of the interaction of the scientific processes to develop even more efficient solver algorithms. This future research will focus on the scientific processes involved with modeling the sequestration of anthropogenic carbon dioxide in the subsurface using the eSTOMP simulator.

Nuclear Science and Engineering

Adaptation of Existing Probabilistic Risk Assessments to Support Reactor Aging Management

Stephen D. Unwin, Peter P. Lowry

◆ Regulatory decision making on reactor life extension is properly risk informed such that reactor aging management and research resources are most effectively expended. The project will establish methods to identify those component aging issues that have the greatest influence on accident and operational risk and determine the most effective maintenance and monitoring strategies as well as materials research priorities for reactor aging management. ◆

Probabilistic risk assessment methodology has provided the principal basis for risk informed decision making in the nuclear power industry. Limitations on conventional methods constrain their value as effective tools to address aging effects and quantify risk and reliability impacts of component aging management strategies. This project will establish a process for expanding the scope and underlying models of an existing probabilistic risk assessment study to allow reactor aging issues to be addressed and alternative aging management strategies to be evaluated and compared. The principal challenge is to model age dependent equipment failure rates and include in the model certain classes of components (principally passive) that have not traditionally been captured in probabilistic risk assessment studies. This is critical because it is passive components generally not amenable to refurbishment or replacement that normally govern accident and operational risks associated with an aging fleet of nuclear power plants.

Probabilistic risk assessment and associated decision technologies will provide framework in which significance of materials reliability issues can be assessed and improvement in structural materials reliability and monitoring methods is identified. Although models have proven a critical information resource in risk informed regulatory decision making, limitations in current methods and models constrain their prospective value in reactor aging management. The objective is to establish a methodological basis for adapting existing probabilistic risk and reliability studies to support integrated reactor aging management programs for passive nuclear power plant components.

We are developing and applying a methodology set to a limited scope probabilistic risk assessment for larger scale models. Software will be created that interfaces with existing assessments to support third party application of methods. Expected outcomes include a documented methodology for augmenting an existing model to allow the risk impact of aging passive components to be determined, alternative aging management strategies to be evaluated, materials research to be prioritized, and a demonstration of methods based on a limited scope model. There are three pillars to the methodology base: 1) a means of screening passive components and associated aging degradation mechanisms to determine which could influence operating risk in an aging reactor, 2) a process to incorporate new failure events systematically into a probabilistic risk assessment, and 3) a method for quantifying importance of components and associated aging stressors to operating risk.

A preliminary activity for FY 2008 was obtaining models and associated plant documentation to initiate methods development. We reconstructed a limited set of models using the SAPHIRE probabilistic risk assessment software and identified and obtained relevant plant system engineering drawings and isometrics to facilitate interpretation of the reconstructed models. An extensive literature review was also conducted. A compendium of documents describing nuclear power plant system and component aging studies, degradation management methods, and risk based methodologies for degradation modeling was the product of this review, which continued in FY 2009.

In FY 2009, a component/aging stressor screening process was developed and applied to limited scope probabilistic risk assessment models. This process drew on results from the Nuclear Regulatory Commission's Proactive Management of Materials Degradation program, where an international expert panel assessed 3500 nuclear power plant component classes against 16 aging degradation mechanisms. Insights of expanded failure modes and effects analysis produced a strong basis for component screening. Also, a new class of risk importance measure was developed that integrates conventional probabilistic risk assessment importance measures with aging susceptibility metrics produced under the materials degradation program. Two publications were prepared describing these new methods, one of which has been accepted to the American Nuclear Society Transactions of the Winter Meeting Risk Management Conference. Significant progress has been achieved on systematic means of identifying appropriate model insertion points and dependences for passive component failure modes associated with aging degradation.

FY 2010 activities will focus on scaling the methodology to broader probabilistic risk assessment models and identifying additional bases for probabilistic quantification and integration of passive component failure modes.

Advanced Radiation Transport Methods

Erin A. Miller, Richard D. Smith, L. Eric Smith, David V. Jordan, Jacob M. Benz,
Christopher J. Gesh, Kenneth D. Jarman, Alex C. Misner, Richard S. Wittman

◆ Because it provides a tool for designing and evaluating detectors as well as interpreting measurements, simulating radiation transport is important for finding or identifying radioactive materials. This project investigates ways of using, combining, and developing radiation transport methods in order to improve these often lengthy calculations. ◆

Radiation measurements are an important component of many security systems, either for detecting radioactive materials or investigating objects (such as with radiography). Most radiation transport simulations are based on a Monte Carlo method, where random individual particles are simulated as they travel through a system and interact. This method works well in many cases but can become prohibitively slow if many particles are involved, as in the case for heavily shielded problems or active interrogation. As an alternative approach, deterministic radiation transport, is based on solving a continuity equation for a steady state particle distribution. Often used for nuclear reactor design, this approach is well suited to describing large numbers of particles.

This project seeks to develop advanced transport methods and approaches based on deterministic or hybrid approaches. Further methods of development offer the possibility of faster simulations, greater solution confidence, and applications of deterministic or hybrid simulations to new problem types. Three main tasks are included: hybrid and adjoint methods, imaging, and deterministic calculation of pulse height tallies. The hybrid methods investigated here use a deterministic adjoint calculation (which reveals the importance of any region of the problem to a detector, as opposed to the count rate due to a source) potentially to improve the efficiency of a Monte Carlo calculation. Adjoint calculations may also be used directly in the attempt to infer source characteristics and location. For imaging applications such as radiography, Monte Carlo calculations can be extremely slow due to the large number of particles. Deterministic methods will be investigated as an alternative. Finally, a new deterministic calculation will be investigated as a possible alternative to a Monte Carlo calculation of a detector pulse height tally.

Two different hybrid methods were identified and investigated. The first method, weight windows, uses an adjoint calculation to improve Monte Carlo calculation efficiency by adjusting particle weights throughout the volume of a calculation. It was found that the adjoint generated weight windows resulted in up to a three times improvement over Monte Carlo alone for problems that included a moderate amount of absorption and scatter but little improvement in problems with less absorption. A second weighting method used an adjoint calculation around a detector to weight a Monte Carlo source surrounding the detector. Again, a benefit was seen only for problems with some absorption, although the improvement was only 20 to 25 percent. In both cases, only a coarse adjoint calculation was needed. A method was also identified for inferring source position and strength based on adjoint calculations and count rates at multiple detectors. This was used to produce a probability map of likely source location and strength and was successfully tested with a simple analytic test problem.

For imaging, deterministic transport has the potential to accelerate cone beam radiography simulations by up to two orders of magnitude over Monte Carlo. However, issues still remain with retaining sufficient spatial resolution in a deterministic calculation. Finally, it was determined that a high degree of angular scattering information must be retained if objects are not highly absorbing. To resolve some issues, a diagram based method for deterministically calculating pulse height tallies was developed. For simple geometries, the method can quickly and accurately compute the photopeak count rate for small detectors, although larger detectors are more problematic. The method has also been extended to include pair production and calculation of the scattered continuum.

Work during FY 2010 will center on several topics. First, the adjoint based source inference work will be extended to use a more complex, computationally determined adjoint and will be applied to more complicated and realistic scenarios. If successful, this work may be useful for scenarios such as locating a source in an urban environment, guiding customs agents in searching a vehicle, or possibly in identifying the contents of a container. Second, both hybrid methods will be applied to more complicated scenarios, when neither deterministic nor Monte Carlo methods alone can solve the problem. One such example is the assay of UF_6 cylinders, which include large amounts of scattering. Finally, the application of hybrid methods to imaging and imaging detectors will be investigated in hopes of determining a more reliable as well as fast method for simulating these problems.

Application of Nitrogen Trifluoride (NF_3) to the Nuclear Fuel Cycle

Randall D. Scheele, Bruce K. McNamara

◆ Actinide and fission product fluoride volatility has long been considered as a potential compact and efficient approach for recovering valuable fuel constituents from spent nuclear fuels. Using nitrogen trifluoride as the fluorinating agent offers the promise of a less hazardous process with another tool to effect separations due to its less aggressive reactivity and thus provides a new and more attractive fuels reprocessing approach. ◆

Under this project, we will develop the thermal chemistry needed to demonstrate the application of a recently identified actinide fluorinating and oxidizing agent to the nuclear fuel cycle. Our focus will be on the fluorinating agent's application to actinide fluoride volatility based reprocessing and to the conversion of reprocessing recovered uranium to uranium hexafluoride for reenrichment. This new actinide fluorinating agent is attractive because it would provide a non-hazardous alternative to highly toxic and reactive tandem fluorinating agents currently used for nuclear fuel cycle applications. It has been demonstrated in scouting thermoanalytical studies to convert effectively uranium metal, common oxides, and fluorides to the volatile uranium hexafluoride with different thermal selectivity. Thermoanalytical, calorimetric, and physiochemical solids characterization techniques will be used to investigate the reaction of the new fluorinating agent with increasingly complex chemical oxide systems representative of used nuclear fuel and its constituents.

This project will determine whether novel new non-hazardous, actinide thermal fluorinating agents can be used to separate and recover valuable constituents in used nuclear fuel using actinide volatility reprocessing. The objective is to determine whether nitrogen trifluoride is an effective fluorinating agent for nuclear materials and fission products, plus whether it could be used as the fluorinating agent in the fluoride volatility fuels reprocessing flowsheet or other portions of the nuclear fuel cycle to produce volatile actinide and fission product fluorides. To investigate, we are using thermoanalytical methods to study nitrogen trifluoride thermal fluorination of uranium, other actinides, and fission product metals, oxides, and fluorides. Ultimately, this project will result in a new thermoanalytical capability to investigate reactions of highly radiotoxic actinides such as plutonium and neptunium. The new thermoanalytical capability will provide an investigatory tool to determine reaction thermal sensitivities and Arrhenius reaction kinetic parameters for reactions of actinide and potentially beta/gamma radionuclides.

As we examined approaches for decontaminating the Portsmouth Gaseous Diffusion Uranium Enrichment Plant in Piketon, OH, we found that nitrogen trifluoride was an effective thermal fluorinating agent for uranium and technetium deposit materials within the enrichment cascade. Nitrogen trifluoride converted uranyl fluoride and various technetium compounds to volatile fluorides. Recognizing that nitrogen trifluoride had potential to be an effective fluorinating agent for producing volatile fluorides from nuclear materials such as uranium, other actinides, and fission product compounds, we began this project to determine if nitrogen trifluoride had an application in the nuclear fuel cycle as a fluorinating agent. Uranium fluoride volatility already has a key role in uranium isotopic enrichment.

During FY 2009, we performed screening studies using simultaneous thermogravimetric and differential thermal analysis to determine the thermal reaction sensitivity and mechanisms of the fluorination of uranium, uranium dioxide, triuranium sequioxide, uranium trioxide, molyb-denum metal and trioxide, ruthenium oxide, and rhodium oxide. Nitrogen trifluoride effectively converted all of the uranium compounds, the molybdenum compounds, and ruthenium oxide to volatile fluorides. Rhodium oxide was fluorinated but did not form its volatile fluoride. The thermal sensitivities differed for the different materials. These experimental studies indicate that nitrogen trifluoride can potentially be used as a fluorinating agent for materials found in the nuclear fuel cycle, including nuclear fuel reprocessing specifically.

In addition to the experimental studies, we installed a simultaneous thermogravimetric and differential thermal analyzer into an actinide glovebox. This new capability will permit us to investigate the fluorination of plutonium, americium, and neptunium compounds to determine whether volatile plutonium and neptunium fluorides can be produced by reaction with nitrogen trifluoride. We published a journal article on the fluorination of uranium compounds.

During FY 2010, we will study the thermal reactivity of the reactions of nitrogen trifluoride with transuranic actinides, use available thermoanalytical methods to develop reaction kinetic parameters for selected reactions, and investigate the fluorination of uranium and fission products or plutonium mixed oxides. The latter is important since doped oxides in a uranium dioxide solution increase the thermodynamic stability of the uranium dioxide, potentially altering the thermal reaction sensitivity of the nitrogen trifluoride fluorination.

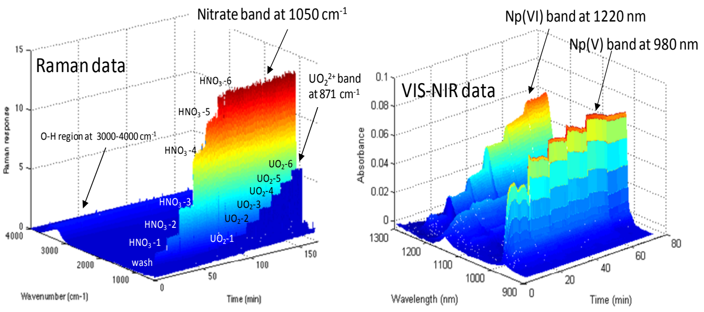
Counter-Current Solvent Extraction Behavior of Neptunium

Brady D. Hanson, Samuel A. Bryan, Justin M. Billing, Gregg J. Lumetta,
Tatiana G. Levitskaia, Amanda J. Casella, Amanda M. Johnsen

◆ Neptunium (Np) is important to high-level waste disposal because of its long half-life. The ability to control and monitor its behavior during recycling processes is imperative in the context of global expansion of nuclear energy. ◆

The recycling of transuranic elements such as Np is a significant means to reduce long-term environmental impact from high level radioactive waste disposal in geologic repositories. This project is studying Np chemistry in transuranic recycle from irradiated nuclear fuel. Np management is critically important in developing and implementing a closed nuclear fuel cycle. The behavior of Np in dynamic solvent extraction systems is difficult to predict because its oxidation state is sensitive to solution conditions. The counter-current solvent extraction experiments performed provided significant insight into Np chemistry under plant prototypic process conditions while demonstrating spectroscopic process monitoring capabilities to enhance process control and diagnosis.

Over the last three years, we installed and instrumented two banks of centrifugal contactors, and a nonradioactive cold and a radioactive hot bank. Cold bank testing involved hydrodynamic leak tests on one bank of four contactors installed in a non radiological fume hood and functional tests of the online spectroscopic instrumentation during flow conditions. The hot bank consists of 16 centrifugal contactors installed in a shielded glove box for use with radioactive materials. The effect of the oxidant pentavalent vanadium on the extraction behavior of Np within a fuel feed tri-butyl-phosphate (TBP)-dodecane solvent system used in the PUREX process was examined. These centrifugal contactor tests provided Raman and vis-NIR spectroscopic data acquired in real-time during the solvent extraction. We envision using the installed solvent extraction test apparatus for online monitoring methodologies for the control and development of spent fuel reprocessing flowsheets.



Several spectral features are apparent within the acquired spectra: in Raman, the water region at 3000-4000 cm^{-1}, the nitrate band at 1050 cm^{-1}, and the UO_2^{2+} at 871 cm^{-1}; in vis-NIR, the ability to monitor both Np(V) at 980 nm and Np(VI) at 1220 nm simultaneously.

Cold tests to show proof-of-principle for real-time measurement of fuel solution components were performed using an aqueous (nitric acid and neodymium nitrate) and organic (TBP-dodecane) phases that were introduced into the extractor bank counter-currently. Spectroscopic probes were positioned to measure aqueous raffinate stream from extractor banks. Cold test conditions were 2 cm centrifugal contactors operated at 3600 rpm and specific aqueous (12 mL/min) and organic (18 mL/min) phase feed rates.

Starting with water and proceeding with gradually increasing concentrations of HNO_3 and neodymium (Nd) ions, about 200 mL of each aqueous solution was delivered through contactors, while the counter-current organic phase delivery was constant. The measured nitrate and Nd concentrations of the solutions were determined using partial least squares analysis of the Raman and vis-NIR spectroscopic data, which were collected in real-time. Nitrate concentration predicted in the raffinate phase mirrored the feed concentration attributed to the insignificant extraction of total nitrate into the organic phase. By contrast, Nd predicted in the raffinate phase showed an appreciable extraction when total nitrate concentration exceeded 1M. Slope analysis (slope = 3) of the distribution values for Nd^{3+} confirmed extraction of a +3 ion by nitrate and verified that the decreased concentration of Nd observed in the raffinate stream (for solutions containing NO_3^- greater than 1M) was due to the enhanced extraction of Nd caused by an increase in total nitrate concentration.

For hot testing, a series of feed solutions containing $UO_2(NO_3)_2$, nitric acid, and Np(V,VI) at variable concentrations were introduced to the centrifugal contactor system to test the functionality of the contactor system with the instrumented spectroscopic equipment. The most concentrated aqueous solutions with and without V added were contacted with TBP-dodecane. Raman and vis-NIR installed inside of the contactor outlet tubing were used to collect spectral data for feed and raffinate solutions in real- time continuously. Np(V, VI) was monitored by vis-NIR spectroscopy. Quantitative extraction of Np(VI) into TPB-dodecane was observed. Addition of V(V) facilitated the conversion of Np(V) to Np(VI) leading to the near complete extraction of Np into the organic phase. Using previously developed Raman chemometric models, a successful quantification of online spectroscopic measurements was achieved; the expected and predicted concentrations of the Raman online measurements show excellent agreement.

Dissolution of Actinides under Oxidizing Conditions for Nuclear Energy Applications

Matthew Douglas, Shane M. Peper, Bruce K. McNamara, Matthew J. O'Hara

◆ With over 20 new nuclear power plants proposed in the United States in the next few years and more than 160 proposed worldwide, it is paramount that efficient, preferably environmentally benign ("green") processes be available to reprocess current and future inventories of commercial spent nuclear fuel. ◆

To date, the Plutonium Uranium Redox EXtraction (PUREX) process is the only technology globally employed at a significant scale to reprocess spent nuclear fuel. This liquid-liquid extraction process uses highly concentrated HNO_3 solutions (6–11 M) at elevated temperatures as the head-end process for dissolving spent nuclear fuel. Following dissolution, organic extractants, such as tributyl phosphate are dissolved in volatile organic solvents and used to facilitate the separation of actinides from each other and other fission products. This process possesses several design shortcomings, such combustible organic solvents and corrosive acids, radiation-induced solvent degradation, loss of minor actinides among fission product waste, and generation of highly radiotoxic mixed waste. We are attempting to recycle uranium by leaching it from the irradiated fuel using optimized process conditions. Removing the uranium will dramatically reduce the amount of radioactive waste requiring long-term storage, because it comprises nearly 94 percent of the total spent nuclear fuel generated by commercial power reactors in the United States.

The work being done under this effort focuses on optimizing the dissolution behavior of U(IV) and other actinide oxides under oxidizing alkaline conditions and understanding the solution and solid-state coordination chemistry in this environment. Fundamental studies will evaluate the use of gaseous reactants to initiate U(IV) oxide dissolution in closed reaction vessels containing aqueous solutions. This environmentally friendly approach results in the generation of benign yet recyclable byproducts such as oxygen, water, and carbon dioxide. The key objective of these studies is to optimize the dissolution of U(IV) oxide under mild conditions at room temperature with the goal of designing an environmentally benign approach suitable for head-end spent nuclear fuel reprocessing. It is anticipated that this technology will be integrated into existing reprocessing flowsheets (such as UREX-1a) or as the basis for developing an entirely green alkaline spent nuclear fuel recycling process. It is anticipated that many seminal scientific contributions will be made in several key areas, including actinide separations and actinide coordination chemistry.

During FY 2009, research was focused in four areas: uranium oxide (UO_2, U_3O_8, and UO_3) dissolution studies, fabrication and testing of an automated system for monitoring actinide oxide dissolutions, solid-state f-element chemistry, and development of a new capability to analyze single crystals containing f-elements spectroscopically. For UO_2, we continued studies from the previous fiscal year and examined the effect of several key experimental parameters on the rate of U dissolution, including peroxide concentration, carbonate countercation, reaction temperature, uranium oxidation state, and carbonate concentration. The purpose of these experiments was to study the optimal reaction conditions to perform a dissolution demonstration using spent nuclear fuel containing approximately 95 percent UO_2. It was found that the ammonium cation yields the most optimal initial U dissolution rates.

Significant work was also done to fabricate, test, and evaluate (using radioactive UO_2 pellet chunks) an automated system for conducting dissolution experiments. We examined the solid-state chemistry of the actinides and lanthanides to determine how they behave following dissolution. Four new crystalline cerium compounds and one new crystalline plutonium compound were synthesized and structurally characterized. The fourth area of research this fiscal year involved the acquisition and testing of a new analytical tool for characterizing samples using Raman spectroscopy. This capability has a microscope platform capable of analyzing single crystals, amorphous powders, and aqueous solutions. All of the cerium crystals synthesized this fiscal year were analyzed with this technology.

For FY 2010, research will continue testing using the automated dissolution system. Specific investigative parameters will include carbonate concentration and countercation, stir rate, and the use of gaseous reactants. Solid-state chemistry studies will be continued for uranium, neptunium, and plutonium, and the microscope-based Raman capability will be moved to a radiologically controlled area so that new actinide compounds can be analyzed by this technique. Additional work will focus on the evaluation of a new class of halide-selective sequestering agents for capturing various iodine species. Iodine is a volatile fission product off-gas that significantly affects the environment at and near reprocessing facilities. Efforts will also focus on developing another analytical capability for radioactive materials, a microscope-based platform for studying solids (both single-crystal and amorphous) and solutions by electronic absorption spectroscopy and classical fluorescence emission spectroscopy.

Dual-Mode Imaging for Dismantlement Transparency

*H. Allen Seifert, Kenneth D. Jarman, Erin A. Miller, Mitchell J. Myjak, W. Karl Pitts,
Sean M. Robinson, Carolyn E. Seifert, Mitchell L. Woodring*

◆ This project investigates the combined use of active radiography and passive gamma ray imaging to verify the contents of storage containers for special nuclear material. The technology would help detect improper material diversion during warhead dismantlement or in various parts of the nuclear fuel cycle. ◆

Nuclear nonproliferation and arms reduction are central objectives of many international treaties and agreements. The signatory nations agree on a process by which to have transparency on all sides. During the process, inspectors might verify that a small number of dismantled warheads are in a set of storage containers, making key measurements to form the basis of comparison for later inspections of equivalent sealed containers. Preventing disclosure of classified information is critical in international agreements, and information barriers are typically established using physical obstructions, instrument firewalls, volatile data storage, rigorous procedural control, and other techniques. The process must achieve a balance between protecting classified data and providing assurances that the system is functioning properly and will faithfully determine whether the container under investigation houses the true item(s).

One method for scanning and verifying sealed container contents is the use of active radiography. An x-ray source is placed on one side of the container, and a large area imaging detector or film is placed on the opposite side. However, this process can provide only the integrated attenuation of the object, not the radioactive makeup of the constituent materials. A second method is passive gamma ray imaging, where emissions from the target object are attenuated and create a projection on a position sensitive detector. The drawback of this method is that a solid mass of nuclear material could be replaced with a lower density form without significantly affecting gamma ray emissions outside the surface, though the absence of material would be detectable with active radiography. Using both active and passive imaging systems would seemingly improve the likelihood of detecting material diversion, as it would be more difficult to “spoof” both systems at the same time. We propose to verify this hypothesis by demonstrating the performance and feasibility of a dual mode imaging system.

To begin, we purchased six epoxy filled Marinelli beakers, three of which had radioactive constituents. The total volume and densities were selected based on parameters of the available radiography systems in the laboratory. The isotope mixture Co-57, Sn-113, and Na-22 was chosen to obtain energies of interest and remain below accountable limits. Additionally, we used a 160-kVp CT radiography system to scan the non radioactive blank phantoms in different positions and orientations. (The radioactive beakers currently cannot be scanned due to building requirements; a second radiography system will become available next year that does not have these restrictions.) A number of other objects such as rubber balls were also scanned to aid algorithm development.

Next, we used a passive radiation imager to construct intensity maps of the Marinelli beakers. Created for the National Nuclear Security Administration’s NA-22 RADMAP project, this imaging system contains a 130 mm position sensitive photomultiplier tube and 900 cm^2 tungsten aperture. We took images of the nonradioactive Marinelli beakers with a point source in the center. Note that the latter setup cannot be distinguished from the radioactive Marinelli beaker using active x-ray imaging techniques alone. Information barrier efforts have focused on evaluating image comparison and analysis metrics and a limited study on integration of active/passive imaging modalities.

We first established a general computational framework for comparing any potential image comparison metric against a set of image data to establish the value of the comparison metrics we devise. We vetted this framework against real data produced from active imaging of test objects with varying density using initial metrics based on comparison of one-dimensional histograms of two-dimensional images. This process provided a level of information barrier through data reduction. We demonstrated the power of metrics to resolve true differences in terms of object densities on several similar objects with varying densities. We then explored a direct active image analysis method designed to estimate the overall density of spherical objects within an image as a means to verify declared materials. Relevant outputs for decisions provide little information about the image as a whole, focusing on limited characteristics of the object of interest. Initial results based on a combination of real images and injected simulated objects suggest that this approach may be a viable alternative or complement to comparison metrics.

Tasks for FY 2010 include further algorithm development and testing, classified simulation work, and further images taken with the active and passive systems. Our ultimate task is to determine requirements for a fieldable system that could be used for warhead dismantlement applications.

Electrochemical Separations for Enhanced Safeguards Analysis

Douglas C. Duckworth, Michael A. Green, Leah M. Arrigo, Martin Liezers, Christopher R. Orton, Scott C. Szechenyi, Matthew Douglas, Shane M. Peper, Jon M. Schwantes

◆ This project supports the safeguards community by providing improved methods for accurate and timely measurement of accountable material mass at fuel reprocessing plants, thereby improving materials control and accountability. ◆

Safeguards accountability at a nuclear fuel reprocessing facility depends on an accurate and timely measurement of accountable material (e.g., plutonium [Pu]) mass in the head-end fuel dissolution tanks and in the various process streams within the remainder of the plant. Current methods are based on destructive analysis of extracted samples, which that can take days to complete and months to verify. The goal of this research is to develop electrochemically "switchable" separations to isolate actinides from reprocessing streams for rapid, non-destructive, and interference-free analysis (neutron, gamma spectroscopy) of accountable materials. The separation relies solely on potentials applied to chemically modified target electrodes. Isolation and preconcentration is achieved by a small voltage step applied to the target electrode to turn on or off the specific actinide affinity of an electrode.

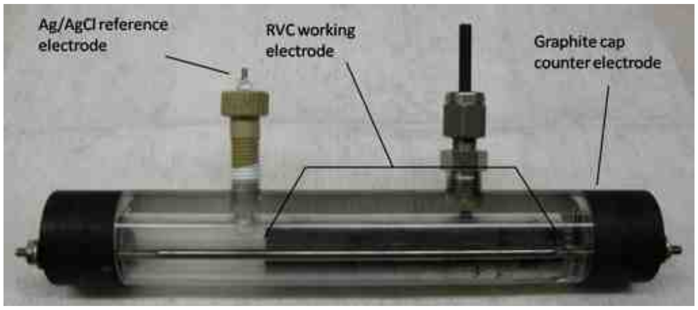
Our approach was to evaluate a well-characterized low surface area flow-by electrochemical cell with dilute dissolver solution. Testing was also began on a large surface area cell and on the use of cells in open-circuit configuration as a sampling device for laboratory based destructive analysis. Project goals were to conduct studies to: 1) scale-up electrochemically modulated separation (EMS) sampling technology, 2) demonstrate operation in complex chemical environments, 3) extend to other elements of interest (e.g., trans-Pu and fission products), and 4) develop and test bench-scale non-destructive analysis and destructive analysis sampling applications for safeguards. These studies aimed to demonstrate the applicability and utility of EMS for safeguards monitoring.

In performing non-destructive analysis (NDA), there is a high level of interference from fission products that do not allow for direct gamma spectroscopic analysis of Pu. Similarly, when analyzing using destructive analysis (DA) methods such as thermal ionization mass spectrometry, Pu must be isolated from other actinides and fission products. The goal of EMS is to provide a simple approach for NDA and DA analysis using Pu isolation and accumulation on an electrode for NDA (or followed by stripping into a clean solution for DA).

Preliminary EMS experiments with spent fuel were performed using a diluted sample of high burn-up (approximately 67 MWd/KgU) boiling water reactor fuel with a 16-year decay time. After EMS separations and fraction collection, the spent fuel fractions were analyzed by both gamma and mass spectrometry. Plutonium was not detected via gamma spectroscopy primarily due to poor Pu accumulation, approximately 5 percent with inductively coupled plasma mass spectrometry (ICP-MS). It should be noted that more than 99 percent of the interfering fission products were not accumulated. Initial tests identified Zr as being strongly competitive, and a large surface area cell was tested as a more promising approach.

The results from the spent fuel test were compared with a similar analysis of a simulated spent nuclear fuel solution. Using a simulated solution that was two orders-of-magnitude more dilute, it was determined that more than 99 percent of the interfering fission products were removed and more than 95 percent of the plutonium was accumulated. Continuing work for FY 2010 will be investigating the role of dilution and inter-element effects on accumulation efficiency.

A custom designed large surface area EMS cell was manufactured and tested with solutions of uranium. This cell was found to accumulate up to 80 percent for uranium when using a reticulated vitreous carbon electrode.



EMS scale-up: large surface area flow-through cell. Reticulated vitreous carbon working electrode has a surface area of approximately 63,000 mm^2.

Experiments were conducted to determine if analyte retention was possible when the cell was at open circuit potentials (i.e., when the EMS cell is disconnected). The small volume cell was used to evaluate uranium retention at open circuit potential. This experiment is important for understanding analyte retention on the surface for the purposes transferring the cell from the sampling site to the laboratory for analysis. After accumulation of uranium, the cell was held at an open circuit potential for 5 minutes. Performed online with ICP-MS, these tests indicated that uranium was retained at open potential. It was also shown that the cell could be successfully migrated to a laboratory setting where uranium could be released and analyzed.

Isotopic Ratio Fluence Monitors for Canadian Deuterium Uranium (CANDU) and Pebble Bed Modular Reactor (PBMR) Plutonium Production Verification

David C. Gerlach, Christopher J. Gesh, Scott C. Szechenyi

◆ This project aims to create monitoring devices that can be attached to reactor vessels and/or individual fuel assemblies, enabling the ability to determine of the amount of plutonium (Pu) produced with sufficient accuracy for safeguards purposes without direct analyses of fuel. The devices will provide a method where adherence to declared reactor operation can be objectively verified. ◆

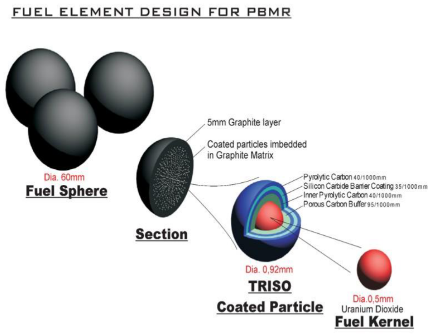
This project builds on past research to develop purpose-built indicators for CANDU and PBMR reactors and fuel assemblies that should make measurement more practical. We will develop and test custom-designed indicators for monitoring neutron fluence exposure and calculating cumulative fuel assembly burnup and total fluence in CANDU and PBMR power reactors. The results will be used to calculate the amount of Pu produced in the CANDU's natural or low-enriched uranium fuel and in the numerous small PBMR fuel pebbles with a degree of precision and uncertainty useful for safeguards verification purposes. The proposed effort should lead to expedient and relatively inexpensive and accurate methods of verifying declared fuel and reactor operations under safeguards for both reactor types.

We have been developing and demonstrating measurement of ratios of relative abundance for certain impurity elements for determining the fluence to which ex-reactor materials have been exposed. Determining fluence allows calculation of the amount of any other isotope produced, including Pu. While it is possible to perform measurements using impurity elements, it is time consuming and would be impractical for large numbers of samples. Our approach to developing the monitoring devices is primarily based on irradiation of candidate materials in the Missouri University Research Reactor (MURR) and examining them at PNNL using the secondary ionization mass spectrometer instrument.

The design of CANDU reactors presents some nonproliferation and safeguard challenges. With respect to material accountancy, the relatively small physical size of CANDU fuel bundles, their short in-core duty cycle, and the ability of the reactor to be reloaded while in operation complicates item accounting considerably compared with the light water reactor (LWR). The low reactivity associated with the use of natural or low enriched uranium fuel limits the discharge burnup of the bundles and increases their throughput rate. Consequently, CANDU reactors are designed for on-line refueling, which can also make irradiation of targets or short-cycling fuel assemblies for Pu production more feasible.

CANDU fuel assemblies.

The PBMR reactors represent less of a proliferation threat but pose safeguard and accounting challenges because of reactor design. The PBMR uses fuel pebbles rather than traditional pellets housed in fuel rods such as an LWR would use. Pebbles contain many coated fuel "kernels" with cores of uranium dioxide with 8 percent ^{235}U formed in a 0.5 mm diameter sphere. The first coating is a layer of porous carbon added using chemical vapor deposition. This layer collects fission products and accommodates deformation of the kernel during the fuel life. The sheer number of fuel elements can present an accountability challenge.



Construction of PBMR fuel elements.

In FY 2009, research focused on potential designs for CANDU monitors and preparing for the irradiation of samples at the MURR reactor. The project team made contact with Canadian personnel involved with CANDU reactor nonproliferation and safeguards, resulting in preliminary mechanical and conceptual designs for a fuel assembly monitor and monitor for the calandria. In September 2009, unirradiated samples of graphite and several candidate metals were shipped from PNNL to MURR. MURR personnel encapsulated the samples and established an irradiation plan by September. In FY 2010, samples irradiated at MURR will be removed at two intervals for analyses, and a final batch will be removed in FY 2011. The samples will be used as reference standards to construct calibration curves for CANDU monitors and develop approaches for PBMR reactor accountability. Preliminary designs for CANDU monitors will be refined, possibly with a trip to Canada for technical discussions with reactor staff.

Multiscale Modeling of Materials Response to Non-Destructive Evaluation Sampling of Reactor Components

Fei Gao, Shenyang Hu, Howard L. Heinisch Jr., Charles H. Henager Jr.

◆ The purpose of this project is to develop a multi-scale approach for modeling and simulating elements of the microstructural evolution of in-core stainless steel reactor components to predict property changes during reactor operation that lead to crack nucleation and high-temperature embrittlement. We will develop accurate predictive models linking microstructural evolution with property changes of reactor materials, which then allows non-destructive evaluation (NDE) methods to sample and deconvolute signals from damaged materials. ◆

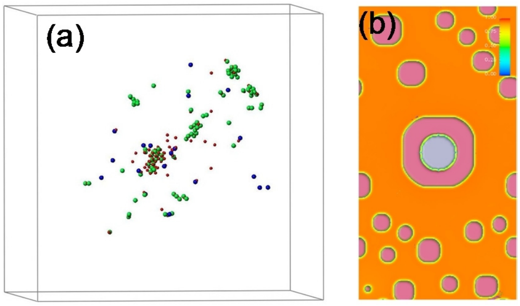
Materials in fission and fusion reactors are subject to continuous time-dependent degradation and aging due to normal service conditions, which significantly affects reactors' safety and lifetime. In order to meet objectives of a materials degradation assessment and management program, one must understand quantitatively the various aspects of damage, damage accumulation, microstructural evolution, and their relationships to potential degradation modes in various materials environments and operating states of the different reactor components. Materials degradation may be assessed based on formulations for various stressor and damage-time relationships or more generally from operating and laboratory experience and engineering judgment.

Enhanced detection capabilities could lead to a more precise mapping, more accurate detection and analysis of large data sets obtained from NDE measurements, and a more precise prediction of degradation over time periods up to 60 years of reactor operation under past and future operating conditions and environments. However, existing monitoring techniques and prediction models do not meet these requirements. As such, an effective scientific approach requires understanding degradation mechanisms, microstructure parameters, microstructure evolution and structure performance, thus identifying the important parameters and dependencies that affect the initiation and development of degradation. The proposed work will combine molecular dynamics simulations, kinetic Monte Carlo techniques, and the phase-field method to understand low-dose and long-time irradiation damage mechanisms coupled with thermal ageing of starting in-core microstructures to predict microstructural evolution during reactor operation.

During FY 2009, we evaluated the existing interatomic potentials for Fe-Cr systems. The existing potentials have been employed to calculate the properties of Cr defects and Cr-vacancy clusters, and their binding behaviors in α-Fe. This potential has been used to study defect generation and defect migration in α-Fe though further modified to consider high energy interactions, and it is smoothly joined by a spline function to the Ziegler-Biersack-Littmark potential.

With this potential, migration mechanisms and corresponding activation energies of Cr-vacancy (Cr-V) clusters and Cr interstitials in α-Fe have been investigated using both the dimer and nudged elastic band methods. The results show that a substitutional Cr atom can migrate to a nearest neighbor vacancy through an energy barrier of 0.56 eV, but this simple mechanism alone is unlikely to lead to the long-distance migration of Cr unless there is a supersaturated concentration of vacancies in the system. The Cr-vacancy clusters can lead to long-distance migration of a Cr atom accomplished by Fe and Cr atoms successively jumping to nearest neighbor vacancy positions, a self-vacancy-assisted migration mechanism. A paper describing these results has been submitted for publication. We have performed extensive MD simulations of defect generation in α-Fe with 10 percent Cr concentration in which the damage in both the bulk and near surface are considered. A total of 40 recoil events for each case were simulated to obtain good statistics. Some Cr interstitials are created as mixed Fe-Cr interstitials and a number of Cr-V clusters of various sizes formed, which may play a significant role in microstructural evolution. These results provide important inputs for the phase field simulation of microstructural evolution.

Unlike the traditional model in which the microstructure evolution is governed exactly by the chemical driving force (the minimization of the total free energy of the system), the defect fluxes in our irradiated systems are driven by both minimization of the total free energy of the system and non-thermal processes such as defect generation, motion, and resolution. The Fe-Cr alloy is used as a model system to demonstrate the application of our phase-field model in predicting the microstructure evolution in materials under irradiation.



(a) Defect distribution in the Fe-10%Cr system, and (b) Phase separation under irradiation.

Nuclear Fuel Cycle Safeguards

Jon R. Phillips, L. Eric Smith, Luke W. Campbell, Alex C. Misner, Jennifer J. Ressler, Norman C. Anheier Jr., Bruce A. Bushaw, Mark C. Phillips, Jennifer E. Tanner, Steven D. Miller, Matthew M. Conrady, Jacob M. Benz, David C. Gerlach

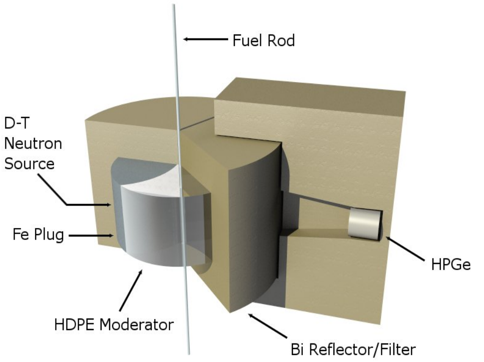
◆ As power production nuclear fuel cycles propagate across the globe, a new generation of measurement technologies is needed to support safeguards monitoring of nuclear reactors and fuel storage, reprocessing, and uranium enrichment facilities. This project will provide a universally applicable method for verification of graphite reactor operation and estimates of plutonium (Pu) production. ◆

The objective of this project is to develop PNNL's capability to address the needs of nuclear fuel cycle safeguards: enhancing of nuclear material safeguards in all aspects of the growing nuclear fuel cycle both in the United States and the world at large. This project addresses the major categories of interest to enhancing the safeguarding of nuclear material in the worldwide nuclear fuel cycle: improving reprocessing, detecting undeclared uranium enrichment, enhancing the tamper resistance of secured enclosures for safeguards equipment, and reconstructing the operating history of research reactors that could have been used for undeclared irradiation of nuclear fuel. All of these objectives are consistent with established DOE/National Nuclear Security Administration policy in support of enhanced nuclear material safeguards and furthering U.S. policy on the nonproliferation of states having nuclear weapons. Effective, efficient safeguards of nuclear fuel cycle facilities are essential as the use of nuclear power grows to meet energy security and carbon management requirements.

Assay of Spent Fuel Plutonium Content. We developed improved methods for quantifying Pu in spent fuel needed to reduce the risk of weapons proliferation. As such, we are developing a rapid, nondestructive method for measuring the Pu content in spent fuel without the need for operator declared information about the fuel. We are also exploring the viability of an active interrogation method high energy delayed gamma spectroscopy (HEDGS) for the assay of spent fuel. The method is based on the detection of delayed gamma rays from fission product nuclei and the unique distribution of fission produced nuclei in three key fissile isotopes (Pu-239, Pu-241, and U-235). Fission is stimulated in the assembly with a beam of interrogating neutrons.

In the first year of this project, we developed a modeling framework that could predict HEDGS signatures for the complex spent fuel environment. The modeling framework developed was created with the goal of post processing flexibility so that a single isotope signature library containing long- and short-lived fission products that define the background and constitute the induced signal could be used to emulate a wide-range of instrument design choices and fuel compositions. Therefore, the modeling framework could support future viability studies of the method, and studies would include exploration of the large HEDGS design space (pulsed neutron source intensity, pulse duration, collimator design, number of spectrometers). In the second year, framework was used to evaluate specific spent fuel assay scenarios. These studies focused on the high energy gamma ray region rather than the lower region often used in spent fuel assay. The higher energy range is attractive for induced signal collection because signal gamma rays are highly penetrating, attenuation is nearly constant, and there is a relatively low passive background from long lived fission products present in the fuel.

Benchmarking measurements for signatures predicted by the HEDGS modeling framework were performed using prompt gamma neutron activation analysis facility at Oregon State University. The measurements utilized a high resolution gamma ray spectrometer viewing a highly enriched uranium foil placed in the path of a collimated thermal neutron beam from the reactor. Results from these measurements show the same prominent peaks in the high energy range as those predicted by the HEDGS modeling. Quantitatively, the measured relative intensities of key lines compared favorably with simulation, indicating that while the HEDGS framework is not yet fully validated, it is suitable for proof-of-principle calculations.



Schematic of the HEDGS system modeled in this study.

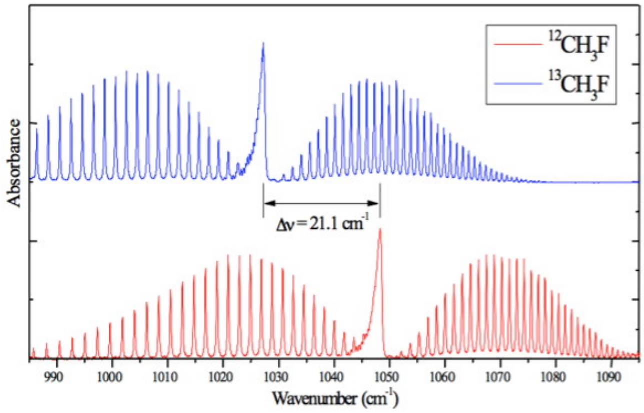
Preliminary viability simulations and analysis performed for the assay of single fuel pins indicate that the HEDGS method is capable of direct Pu isotope assay with uncertainties less than the 10 percent typical of today's confirmatory method without the need for operator declared information about fuel that confirmatory methods require. Therefore, the method appears promising to meeting international safeguards objectives in spent fuel assay: improved accuracy, independence from operator declarations, and timeliness. Further work (simulation and measurements) is needed for a definitive assessment of the method, and the modeling framework developed by this project will be a key enabler for that future study.

Detection of Highly Enriched Uranium Production in Enrichment Plants. We developed a new approach to detect rapidly undeclared production of highly enriched uranium (HEU) in plants under inspection. The current “gold standard” approach relies on off site analysis in a network of analytical laboratories (NWAL) to detect the dilute presence of HEU particles in environmental samples. While environmental sampling and follow-up characterization by NWAL has high probability of detecting HEU production within a low enriched uranium facility, swipe sample monitoring is subject to collection variability and the time to results is very long compared to the International Atomic Energy Agency (IAEA) timeliness goal of less than one month. NWAL analysis typically requires 2 to 12 months from sampling to results.

Our task had two parts. Part 1 developed a tunable quantum cascade laser spectroscopy technology to provide continuous integrated safeguards monitoring of $^{235}UF_6/^{238}UF_6$ isotopic ratios within isotope separation facilities. Rapid in-line determination of isotopic ratios would enable new capabilities in uranium isotopic monitoring at declared facilities. Part 2 evaluated the laser ablation absorbance ratio spectrometry (LAARS) for highly enriched uranium particle detection within uranium enrichment plants. An automated, unattended environmental aerosol sample collection approach will be developed and combined with the uranium isotope ratio analysis system to detect enrichment facility misuse in a timely manner.

Part 1 demonstrated isotopic characterization using external cavity quantum cascade laser spectroscopy techniques for gaseous uranium hexafluoride (UF_6) isotope characterization. Two UF_6 surrogate gases were identified and one was analyzed. The measurement targeted the carbon atom in natural (1.1 percent ^{13}C, 98.9 percent ^{12}C) and isotopically enriched (99 percent ^{13}C) fluoromethane (CH_3F). An abundance uncertainty estimate was found to be 1±6 percent with an enrichment ratio ($^{13}C/^{12}C$) detection limit of 0.06 percent. The ability to measure enrichment levels in gaseous CH_3F provides compelling evidence that this technique could be applied to UF_6 safeguards monitoring applications.

Part 2 evaluated the feasibility to use LAARS as part of a purpose built uranium enrichment facility safeguards technology. A laboratory research grade aerosol generator/collector was developed to provide a testbed that facilitates aerosol particle generation and characterization. A state-of-the-art miniature ablation laser was identified. A stabilized laser diode incorporating a volume holographic grating was evaluated for performing enrichment spectroscopy. We demonstrated for the first time rapid isotopic analysis on single 1 μm diameter particles using the LAARS measurement system. The viability of the method to complete 100,000s of single particle measurements on a surface accurately within about 15 minutes was demonstrated. This was a key result that demonstrated the feasibility of rapidly performing in facility isotopic analysis on collected aerosol samples. The technical results of this study in a paper and presentation were delivered to the Institute of Nuclear Materials Management 50th annual meeting in Tucson, AZ.



Isotopic specific vibrationally shifted gaseous fluoromethane spectra.

Improvements in Tamper Resistant Containers Used in Safeguards Systems. We developed optically stimulated luminescent (OSL) paints for application to tamper resistant containers. Containment verification is a high priority for safeguards containment and surveillance. Nuclear material containers, safeguards equipment cabinets, camera housings, and detector cable conduit are all vulnerable to nefarious tampering. Additionally, critical safeguards material, equipment, and data are stored in enclosures at the site of an inspected facility, providing ample opportunity to tamper with equipment and/or data give false information. Protecting and verifying integrity of these enclosures and developing techniques and procedures for containment verification is vital to IAEA goals. This task explores a passive approach by incorporating OSL material into paint that can be applied to container surfaces. The introduction of OSL paint provides another level of security to verify that a container has not been tampered with.

Current inspections of nuclear material containers and equipment cabinets/conduit involve a visual inspection of accessible surfaces and interrogation of any tamper indicating devices used on lids/doors. In most cases, a tactile inspection is not practical or performed. Adding a special coating to containers, cabinets, and conduit is attractive because it is a passive approach and can be easily implemented with new enclosures to existing cabinets and conduit already deployed. The coatings containing OSL material are very difficult to counterfeit. OSL materials are phosphors that luminesce in proportion to the ionizing radiation dose stimulated with specific optical wavelengths. Also, the presence of pre-irradiated OSL material on a surface can indicate that the integrity of the surface is intact. The OSL material used is proprietary and not commercially available.

This project explored the viability of introducing OSL material into powder paint, similar to that used by the IAEA. Lithium fluoride (LiF) was chosen as the OSL material, and initial work centered on testing various formulations, particle sizes, and loadings of LiF in combination with coating material. Small glass slides provided the surface. Once this aspect was optimized, work began on coating, tampering, and repairing larger (1 ft^2) metal sheets. Interrogation of the OSL coatings also progressed from using a fixed scientific grade charge coupled device to a more mobile COTS Fuji ultraviolet/infrared (IR) camera. The first year focused on developing the process and application of introducing OSL material into powder paint and onto a surface. Testing involved many different formulations for preparing, producing, and applying the LiF and powder paint mixture. By the end of the first year, this process had been optimized.

At the beginning of the second year, experimentation began on interrogation of the coatings. The first step was to determine the optimal emission wavelength. Results settled on the infrared peak, and optimization focused on the excitation wavelength. It was determined that the blue wavelength (450 nm) generated the largest signal from the OSL material. Two delivery methods were explored: high intensity short burst (flash) or a continuous wavelength light (LED cluster). A flash would impart the greatest amount of energy in the shortest amount of time, providing the best signal to noise ratio. Most flash lamps, however, generate a large amount of IR, imparting a lot of noise into the measurement. A large number of infrared cut filters were required that significantly decreased flash efficiency, leading researchers to focus on continuous wavelength light. While not as intense, there was little infrared produced, and a blue LED cluster negated need for a blue centered bandpass filter (as was needed for flash) and provided a clean excitation source. The final step was to create, tamper, and repair the metal sheets, the next logical step in moving toward tampering with IAEA equipment cabinet. A number of sheets were created with a variety of hole sizes and orientations.

From interrogation of the tampered/repaired sheets, further optimization of the infrared region was required. It was determined that the silicon based CCD cameras were ill suited for interrogation in the infrared spectrum. Additionally, the material that had been coated onto the metal sheets was not infrared grade OSL. Future study will focus on tools necessary to optimize interrogation in the infrared spectrum: acquiring an InGaAs camera, use of infrared grade OSL material, and optimized readout in the infrared region.

Development of a New Method to Measure Plutonium Production in Graphite Reactors. We developed an additional method to quantify Pu production indirectly in graphite moderated reactors that can be applied in future verification and analysis. It may also lead to a method of nuclear material accountancy for the relatively new pebble bed modular reactor (PBMR). The task mainly developed separation and analysis methods for trace levels of beryllium (Be) isotopes generated in fuel channel materials in graphite moderated reactors. The Be levels generated provide a method of accurately estimated Pu produced in fuels without depending on preexisting impurity elements in the graphite or on direct analysis of spent fuels, as pursued in previous related projects at PNNL. Analyses of trace levels of Be isotopes in environmental samples has been aimed at determining flux of cosmogenically produced amounts of ^{10}Be rather than that produced by neutron fluence exposured of graphite in a reactor. With the exception of a single study utilizing secondary ion mass spectrometry (SIMS) to analyze Be isotopes in environmental or geological samples (which was not pursued further), these analyses have usually been conducted using accelerator mass spectrometry, an expensive method performed at only a few laboratories.

The chief accomplishment of this effort was that a rigorous, low blank, reliable method was developed to separate chemically picogram to nanogram amounts of ^{9}Be and ^{10}Be from graphite, necessary due to close, unresolvable atomic weights of ^{10}Be and ^{10}B. The method was combined with one currently in use to separate select actinide elements to maximize the use of small graphite samples. A method for analysis was also developed to measure precisely amounts of each Be isotope and the ^{9}Be/^{10}Be ratio by SIMS. Several samples from a low and high burn-up graphite reactor were processed and analyzed. Trace amounts of U in graphite were found to generate Pu, Be, U; Pu were separated from samples for analysis by SIMS (Be); and the U and Pu isotopes were analyzed by thermal ionization mass spectrometry. The correlation of Be abundances with U and Pu isotopes confirmed the utility of this approach in quantifying Pu produced in fuel rods based on Be (and trace U and Pu) isotopes measured in samples taken from adjacent graphite fuel channels.

Results will be used in a new project to develop a simple, direct SIMS analysis method, circumventing chemical separation for possible application to graphite samples from PBMR safeguards. Methods developed will also be applied to future case studies of graphite moderated reactors for safeguards verification. Analyzing changes in selected isotope ratios to estimate Pu production (of which the Be study is a subset) will be pursued to develop low cost, easily analyzed small monitoring devices for CANDU reactors.

On-Line Flaw Detection in Reactor Piping using Acoustic Emission and Guided Wave Ultrasonic Techniques

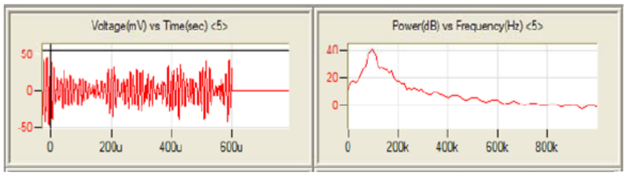
Stephen E. Cumblidge, Steven R. Doctor

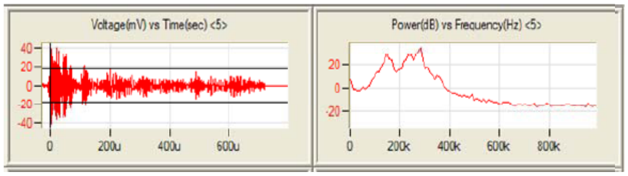
◆ A move from periodic local inspections of welds to global continuous monitoring would greatly improve crack detection, especially for the fast-growing flaws. An effective, online, continuous monitoring of the pressure vessel and important Class 1 piping systems using acoustic emission and guided wave ultrasound may be able to detect the fast-growing cracks and notify the reactor operators before the cracks have an opportunity to cause a leak in the reactor components. ◆

A combination of acoustic emission and guided wave ultrasound can be used to monitor a reactor for cracking in two ways. Acoustic emission sensors can passively listen for characteristic signs of cracking during reactor operation. With an array of sensors mounted in strategic locations, one can determine the approximate location of the cracking as well. The same sensors may possibly be used in an "active" mode, whereby they send out ultrasonic signals that travel down piping as guided waves. These guided waves would be emitted at regular intervals, and specific changes in the reflected and transmitted guided waves would show signs of degradation. While both acoustic emission and guided wave ultrasound have been well developed, they have not yet been used together for continuous online monitoring of nuclear components. This project will experiment with these techniques to allow for continuous on-line monitoring of reactor components for cracking.

After researching the best acoustic emission systems, an 8-channel micro-DiSP acoustic emission system was purchased from Physical Acoustics that allows waveform capture and real-time analysis of acoustic emission signals. After the system was installed and its capabilities determined, it was tested on a full-sized mock-up of a reactor pipe. The specimen used for this experiment was a large-diameter pipe from a cancelled nuclear power plant. The test consisted of standard pencil-lead breaks and fatigue cracking of surrogate samples that were attached to the pipe. With accuracy, the system was able to determine the locations of the events and could discern between fatigue flaws and background noise.

The next test consisted of growing a fatigue crack in situ using a four-point bend testing system. The transducers were attached to a 4-inch diameter pipe. A notch was introduced into the pipe, which was then cycled 600,000 times at loads ranging from 2000 to 10,000 pounds. These initial cycles allowed for the measurement and characterization of the noise generated by the fretting at the four loading points. When the crack began to propagate, it was detectable. The fretting noise typically has a center frequency of 100 kHz, and fatigue cracks have a center frequency of 170 kHz. The graphic shows the waveforms and Fourier analysis of the fretting signals and the acoustic emission events produced by fatigue cracking in the carbon steel pipes.


Fretting Noise


Fatigue Crack AE Signals

Fretting noise and acoustic emission signals in carbon steel.

The acoustic emission work has been an important part of PNNL's university engagement. PNNL has received invitations to two workshops held at the Pennsylvania State University in 2009. The first was the Workshop on Robust and Autonomous Ultrasonic Toolsets in February, and the second was the Structural Health Monitoring for the Nuclear Industry Workshop on Structural Health Monitoring in June. A presentation that included the acoustic emission work was presented at each workshop. The acoustic emission work was also discussed in a peer-reviewed publication at the International Conference on Nuclear Engineering 17 Conference in Brussels, Belgium in July. An abstract based on the acoustic emission work has been accepted for the American Nuclear Society winter meeting in November.

For FY 2010, our work on producing and measuring the growth of fatigue flaws will be expanded. The use of waveguides to filter extraneous noise will also be explored. Additionally, stress corrosion cracks will be grown in Alloy 600 and 690 materials to compare the acoustic emission events produced by cracking in these materials.

Spent Fuel Shipping and Storage Cask Monitor

John A. Dorian, James R. Skorpik

◆ This project aimed to develop a design to observe the location and status of casks used for long-term storage of spent nuclear fuel. Such a device would enable authorities to monitor individual casks in near real-time and collect data relevant to each cask. ◆

A labor-saving, cost-effective system is desired to ascertain continuity of knowledge of spent nuclear fuel (material) stored within a dry storage cask or container. Trends of increasing energy demand, difficulty to acquire clean fossil fuel and environmental concerns to diminish carbon dioxide give credibility to an expanding global nuclear power industry that is expected to escalate generation and storage of material. In contrast, resources to monitor such material remain essentially constant. A long-term projection is that developing nations desiring the benefits of abundant sources of clean, safe nuclear energy will contribute to this movement but simultaneously increase the need for improved material safeguards. Clearly, a method that improves the practice of ascertaining material continuity of knowledge while reducing inspector labor and radiation exposure will be needed.

Our concept was to implement data logging and remote monitoring of individual containers. If designed and implemented sensibly, the following advantages would be achieved: 1) a dramatic improvement in the rate at which material continuity of knowledge state is ascertained, 2) the monitoring of containers during transit and interim storage, 3) the ability to flag a change (if detected) and enable a timely response, 4) the increase of inspection efficiency, reduction of inspector exposure to radiation, and reduction of labor, and 5) reduction of intrusiveness to nuclear facility operation.

Material containment and surveillance has been used by the International Atomic Energy Agency (IAEA) to maintain continuity of knowledge on material that it has accepted for inspection under a country's Comprehensive Safeguards Agreement. Combined with host nation declarations and physical inspections, monitoring technologies provide the basis to draw independent conclusions about material location and status. Minimum requirements included the following: 1) sensitivity to cask lid and body motion associated with moving or opening the cask to provide a "tamper indicating seal," 2) detection of vibration or shock associated with cutting into the cask to bypass opening the lid or tampering with the device, providing surveillance of containment integrity, 3) a uniquely identifiable device, and 4) security of a radio frequency capability to allow for rapid interrogation of collected data. Currently, IAEA inspectors apply seals to a container and thereafter periodically conduct on-site visits to inspect the seals. The timeliness of the inspection rate is dependent on fuel characteristics but is typically a twelve-month period.

Previous efforts have included an authenticated tracking and monitoring system (ATMS) and the 3013 container surveillance system. An ATMS demonstration used a truck with trailer and monitored temperatures, fiber optic seals, system voltages, location by means of the global positioning system, and communication by satellite. A remote 3013 container surveillance system monitored internal gas pressure by a magnetically coupled sensor, temperatures, three-axis accelerometer (shock), and a mechanical tamper switch. Data were conveyed by a wireless radio frequency link to a tag reader placed in the vault to monitor up to 28 individual radio frequency links.

During FY 2008, the project primarily addressed potential sensing technologies for interim storage containers. Work included evaluations to determine needed sensor attributes for a data logging and monitoring system and the diversity of container-overpack assemblies. A presentation was given at the annual meeting of the Institute of Nuclear Materials Management, and a paper by the same title was published as a portion of the conference proceedings. Two site visits were also conducted early in the project to become familiar with both different designs of spent nuclear fuel containers and the environment that such a system would need to operate.

Several technology gaps for a container monitor existed for a solution comprised of an integrated complement of sensors specific to spent nuclear fuel. In FY 2009, work primarily prioritized technologies suitable for rapid demonstration of monitoring interim storage containers, low-power configurations, and minimal data security. Prior to early curtailment, tasks included a laboratory demonstration of the sensor, radio frequency identification tag, and data collection application. A literature review suggested ranges of shock measurement related to movement. The key issues identified for the system included sensing parameters, mechanism for attachment to the cask, internal power devices, sensor recording, and communications network protocols. No further research was conducted on the project, and was completed in March 2009.

Theoretical Modeling and Ex-Reactor Testing of Fuel Properties to Accelerate Fuel Qualification

Carl E. Beyer, Brady D. Hanson, Andrew M. Casella, Rick E. Williford, Kenneth J. Geelhood

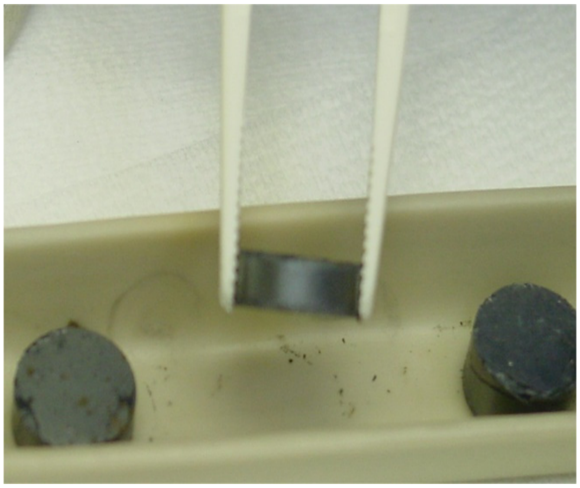
◆ This project is intended to shorten fuel development and qualification time by providing better data early in the program as opposed to waiting for completion of lengthy irradiation test campaigns. ◆

There is renewed U.S. interest in expanding its use of clean, safe nuclear power for domestic needs. Likewise, the rest of the world is considering the expansion of nuclear power as part of an effort to meet growing energy needs while minimizing carbon dioxide emissions. The Global Nuclear Energy Partnership (GNEP) program bears witness to these renewed interests in nuclear power. One aspect of GNEP is the development of advanced burner reactors (ABRs) to recycle spent fuel from the existing worldwide fleet of light water reactors (LWRs). The primary fuel types identified for the ABR is either oxide or metal fuel with minor actinides. Additionally, DOE is pursuing the Generation IV Nuclear Energy Systems Initiative, which is aimed at developing and demonstrating advanced nuclear energy systems that can meet future needs for safe, sustainable, environmentally responsible, economical, proliferation-resistant and physically secure energy. Under the GenIV initiative, the very high temperature and supercritical water cooled reactors were considered, both of which offer greater overall efficiencies and enable the production of hydrogen for use in the transportation industry as well as the gas, lead, and sodium cooled fast reactors.

Our research is focused on two goals to assist in accelerating the qualification of new fuel types for new reactors: advancing the science of nuclear fuel performance modeling by developing first principle (theoretical) models and developing out of reactor testing capabilities to verify theoretical models and screen new fuel types utilizing a unique irradiated fuel (RADFUEL) concept for early modeling and simulation activities in support of in reactor testing campaigns. The latter goal will assist in demonstrating the theoretical modeling is valid. Overall, this project intends to demonstrate PNNL's ability to accelerate fuel development and qualification for transuranic fuel to be burned in the proposed advanced recycle reactor.

The first goal of the project will result in a theoretical model for fuel thermal conductivity for mixed oxide fuel containing minor actinides. The second goal is to develop and refine the capability to fabricate (on a small scale) and characterize fuels, including advanced fuels for any of the proposed reactor types prior to irradiation and RADFUELs to simulate advanced fuels at various fuel burn up conditions to support fuel performance modeling needs in advance of in reactor testing. While the initial focus has been on oxide fuels, the methodology and processes developed may be expanded for other fuel types. These data and model development are intended to advance the modeling efforts for new fuel types.

Modeling activities performed throughout FY 2009 included developing atomic potentials for fission products to be used in the atomistic calculations to determine thermal diffusivity and thermal conductivity of irradiated oxide fuels. A model was developed for irradiated fuel based on these calculations. Our experimental activities concentrated on pellet fabrication and installing the Netzsch laser flash analyzer in a radiologic fume hood for measuring the thermal diffusivity of RADFUELs. Additionally, pellets of uranium dioxide were successfully fabricated.



Uranium dioxide sintered pellets fabricated at PNNL.

Once the fabrication technique is properly refined during FY 2010, RADFUELs containing low levels of minor actinides, such as in traditional spent LWR fuels, will be fabricated and characterized. The concentrations of the minor actinides will be increased to simulate the proposed composition of fuels for fast reactor fuels. FY 2010 will also include providing fuels to the project examining fuel/cladding compatibility for their use and testing to determine fuel compatibility with reactor coolants using the experience with leach testing in support of geologic disposal but under reactor operating conditions.

Physics

Advanced Computing Architectures for Smart Sensors and Sensor Analytics

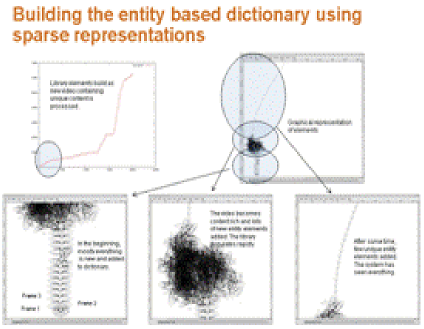
Harold E. Trease, Paul E. Keller, Brett G. Amidan, Andrew J. Stevens, Ronald C. Taylor

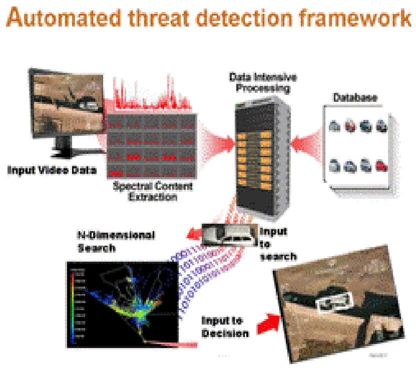
◆ This project will demonstrate the utility of building smart sensors that integrate modern low cost, low power computational processing capability directly with sensors, where computational resources are integrated with sensors for generating intelligently compressed signatures and performing data fusion at data acquisition and/or at the centralized computing facilities. ◆

The amount of image data generated by airborne and remote sensor platforms is growing exponentially. For example, a single unmanned air vehicle platform may consume the entire bandwidth capacity of one satellite. Data are increasing at such a rate that communication, storage, and processing capabilities are overwhelmed to the point that sensor data is collected but never analyzed or in some cases not stored. This problem will get exponentially worse with future unmanned air vehicle platforms that provide wide area surveillance capability through arrays of sensors, swarms of networked sensors, and multisensor platforms. Even if all the raw data could be communicated to a terrestrial analysis center, there is insufficient time to analyze it using manual procedures. New software algorithms and advanced processing hardware must be explored to extract useful information from this explosion of sensor based information. This would provide advanced data processing at the point of acquisition, where the analyst would get a data summary without the need for access to the volumes of original raw data.

This project will demonstrate the application and utility of advanced computing architectures in the areas of smart sensors, sensor analytics, and sensor integration. The proposed advanced architectures will be based on modern multicore commodity processor building blocks with areas of application including radiation sensors and sensor networks, video surveillance networks, and swarming (i.e., coordinated, networked) unmanned air vehicle platforms. Combining these two technologies (i.e., powerful, mobile, efficient computing platforms with distributed sensor networks) will demonstrate the utility of smart sensor technology for new sensor design to take advantage of on board, mobile, low cost computational capabilities. We have explored a new integrated platform consisting of three major components: sensor hardware, processing algorithms, and advanced micro computing architectures. Our platform takes advantage of a new sensor/algorithm processing paradigm called compressive sensing. We add modern low power, high performance parallel processing hardware to address the throughput issue. This enables us accelerate the throughput of the sensor by using Moore's Law for semiconductors (based on computing capability growing exponentially) in conjunction sensor to form a better sensing platform.

Compressive sensing uses a concept called sparse representations to adaptively construct a map of the sparse patterns contained in the sensor output, where the sparseness pattern identifies components of the sensor data that contains valuable sensor information. Through use of compressive sensing and sparse representations, we can process information on remote platforms and transmit only the data summarization to analysts, where it is a fraction of the original raw data but contains the basic information content.





At a high level, the presentation above contains a description of a new integrated sensor, data processing, and computer hardware system based on compressive sensing and advanced micro computer architectures.

During FY 2009, we constructed a processing system to demonstrate the concepts of integrating compressive sensing, sparse representation, and micro computer architectures using video data as senor data, a portable computer as the remote computing platform, and an Android cell phone as the client device that communicates with the sensor platform. The major results include successful unmanned air vehicle processing and surveillance video capabilities.

Develop Ar-37 Measurement Capability for Treaty Verification Applications

John L. Orrell, Craig E. Aalseth, Derek A. Haas, Martin E. Keillor, H. Allen Seifert

◆ A capability to measure precisely the radioactive noble gas argon (Ar)-37 will enhance the nation's ability to detect underground nuclear weapon testing. Development of specialized radiation detector equipment to measure Ar-37 in trace quantities supports this objective. The science and technological basis that this work will support a broader objective of monitoring and deterring international nuclear weapon proliferation. ◆

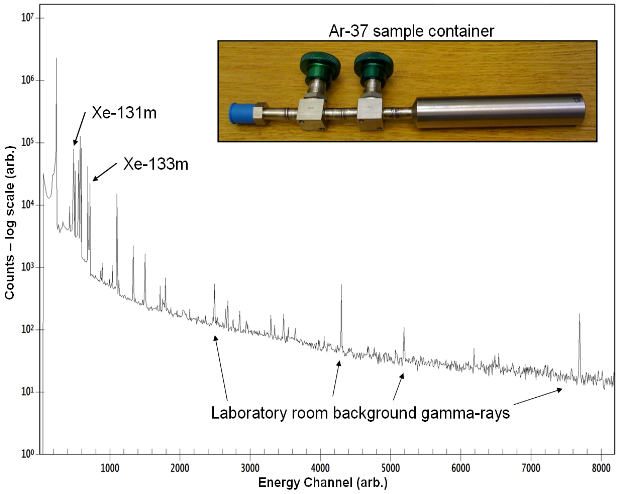
In the Comprehensive Nuclear-Test-Ban Treaty that provides the basis for the onsite inspection of suspected nuclear facilities, Ar-37 has been identified as a relevant isotope for measurement. It is not produced in quantity at nuclear reactors or in the atmosphere but does appear in subsurface nuclear explosions due to the interaction of neutrons with calcium. This project will develop a basis for a future laboratory capability for Ar-37 measurement, a prerequisite for advancing the state-of-the-art in technology applied to onsite inspection in treaty verification regimes. This project advances these goals by combining prior work on low background proportional counter development and energy threshold reduction. The outcome of this work will be a demonstrated detection apparatus focused on laboratory measurement of Ar-37. Included in this outcome is the specified measurement sensitivity quantified as the minimum detectable concentration of Ar-37 in the detection instrument. Estimations for improvement to the sensitivity of the apparatus and assessment of the apparatus as a field instrument will be reported.

The measurement of Ar-37 is challenging because it only emits difficult to detect low energy x-rays. The method of measurement relies on high sensitivity gas proportional counters. At present, only the Swiss and Chinese possess dedicated gas proportional counter equipment capable of measuring Ar-37. Development of an ultra-low radioactive background gas proportional counter at PNNL is hoped to provide the ability to measure Ar-37. Given adequate shielding, the ultra-low radioactive background nature of the gas proportional counter construction should allow for attempting the world's most sensitive measurement of Ar-37. However, the primary development objective of this project is to prepare a laboratory based Ar-37 measurement capability relevant to international treaty monitoring.

During FY 2009, research focused on production handling of the Ar-37 gas. Ar-37 is not naturally available in sufficient quantities for measurement due to its brief, 35 day half life. For this reason, Ar-37 is created using neutron irradiation at a nuclear reactor. There are two methods of generating radioactive gas in sufficient quantities for Ar-37 measurement: neutron irradiation of Ca-40 and neutron irradiation of natural argon gas. The University of Texas worked with PNNL to develop the ability to irradiate natural argon gas and provide a sample for Ar-37 for measurement in a gas proportional counter.

The first Ar-37 sample was received at PNNL in August 2009. Unfortunately, a preliminary measurement using a high purity germanium gamma ray spectrometer revealed the presence of unwanted radioactive xenon gas in the sample cylinder. It must be noted that xenon gamma rays are roughly 100 times as energetic as the x-ray emissions from Ar-37. For this reason as well as for maintaining a pure argon environment inside the gas proportional counter, an Ar-37 measurement using the ultra low radioactive background gas proportional counter was not attempted during the current fiscal year.

In FY 2010, work will refocus on obtaining a usable sample of Ar-37. As the reliability of the Ar-37 source improves, the effort direction will shift to determining the level of Ar-37 sensitivity achievable with the ultra-low radioactive background gas proportional counter. Efforts will also broaden to include developing secondary methods of neutron irradiation for generating Ar-37 from other materials. Work with the gas proportional counter will focus on improving the low energy measurement sensitivity (i.e., detector energy threshold) needed to detector the Ar-37 decays. Finally, a concept for an Ar-37 measurement system will be prepared in a white paper format.



Gamma ray spectrum measured from the Ar-37 sample container with a high purity germanium detector indicating the first radioargon sample is contaminated with radioxenon isotopes.

First Operation of a Novel, High Mass Detector as a Weakly Interacting Massive Particle (WIMP) Dark Matter Detector

Martin E. Keillor, John L. Orrell, Erin S. Fuller

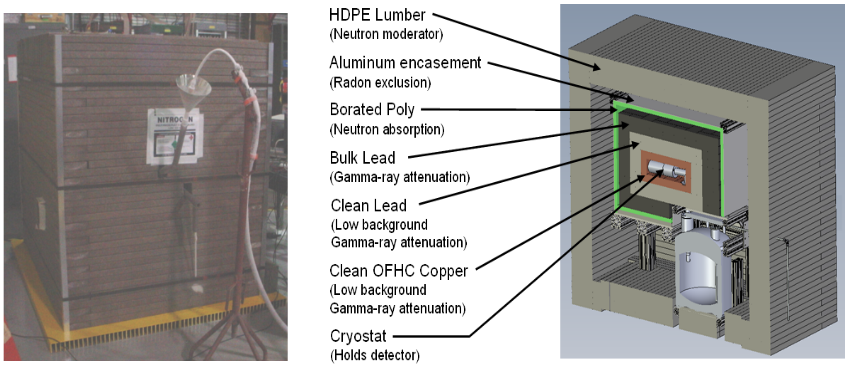
◆ Our project will collect and analyze data covering a low energy region not previously explored with large high purity germanium spectrometers. We will assess this new detector technology for future large-scale WIMP dark matter searches. ◆

Public and scientific interest in dark matter stems from the our knowledge and understanding of approximately 5 percent of the universe's composition. Direct detection of dark matter particles is perhaps the single most pressing astroparticle physics measurement sought by cosmologists and theoretical particle physicists alike. Theoreticians postulate the existence of a WIMP whose gravitational influence is ubiquitous but otherwise does not participate in familiar interactions of the standard model of particle physics. Dark matter is better understood—perhaps better constrained—of major unknown categories. The search for WIMP dark matter has more than a decade of history, dove-tailing on efforts of cosmologists to account for the evolution of the mass distribution of the universe. Where these observations have led to the proposal of an astroparticle solution, a confrontation with the standard model of particle physics is inevitable. No known particle has properties that account for astronomical observations, yet a clear prediction emerges that WIMP dark matter should interact with the matter of our everyday experience via elastic scattering.

This project is based on recognition of an advance in low energy threshold (about 0.3 keV) germanium detector technology. A low energy threshold can exploit the exponential increase in WIMP signal by measuring decreasingly energetic nuclear scattering recoils. We will identify backgrounds to the WIMP signature and investigate a region of WIMP mass and interaction cross-section not excluded by current experiments. Measurements are expected to cover the region of the disputed positive result reported by the DAMA Collaboration.

This project made use of a low background detector shield that was designed in FY 2008 and was physically installed at northern Minnesota's Soudan Underground Laboratory in early FY 2009. Additionally, the PNNL owned low energy threshold germanium detector was installed inside the shield at Soudan. The germanium detector was operated for four months to assess the status of the low background shield, the data acquisition system, and the performance of the detector itself. Conclusions from this work were as follows: 1) the low background shield was successful (i.e., contained a sufficiently low background), 2) the data acquisition system was less than ideal (i.e., it did not have a low enough energy threshold), and 3) the detector itself was the greatest source of unwanted natural radioactivity.

To improve performance of the data acquisition system, a collaborative effort with the University of Washington was initiated. The university has a highly configurable research grade pulse shape digitization data acquisition system. It is also a project research objective to develop an all digital data acquisition system superior to any comparable low energy threshold analog data acquisition system. For example, recording pulse shapes has allowed for identification of off-normal signal pulses from the germanium detector. An analog data acquisition system would not have allowed for identification of this potential issue in detector performance of a newly produced detector design. To address the issue of the level of natural radioactive content of the detector system, another collaborative institutional effort was initiated with the University of Chicago to install a recently produced, improved, and much lower radioactive content low energy threshold germanium detector at the Soudan. This improved detector was installed underground in the PNNL low background shield in August 2009.



The underground shield for the low energy threshold germanium detector and a cut away schematic view.

For FY 2010, we will continue with the demonstrated low background system capable of improving on dark matter exclusion limits. It is anticipated that six months of study will lead to further improvements to the exclusion limits on the properties of dark matter.

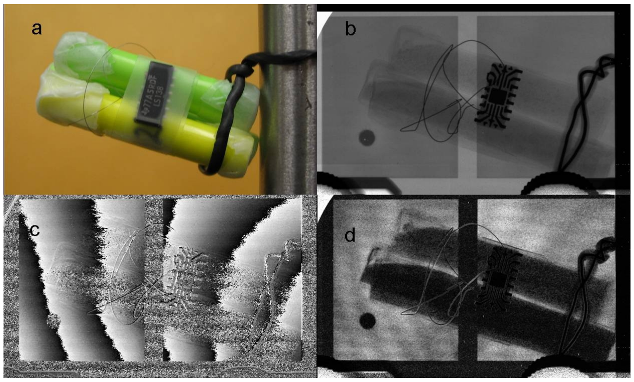
Phase Contrast X-Ray Imaging for Enhanced Explosives Detection

Erin A. Miller, H. Allen Seifert

◆ Phase contrast x-ray imaging is based on local variations in an object's x-ray index of refraction rather than its absorption to produce contrast. This allows for objects with very little x-ray absorption to be imaged. Our research will verify a new technique for performing phase contrast imaging and evaluate the efficacy of the technique for the detection of explosives. ◆

Phase contrast x-ray imaging is similar to conventional x-ray imaging, but the image contrast is produced by local variations in the object's x-ray index of refraction rather than its absorption. The technique has been used for several years with synchrotron x-ray sources, where it has been of great use for imaging low density and low *Z* samples such as biological specimens or polymers. Operational applications incompatible with synchrotron sources have been limited due to stringent source coherence requirements. Recent work has demonstrated a new phase contrast imaging technique that allows the use of a conventional x-ray source. Throughout this approach, a series of gratings is used to improve the x-ray source characteristics, set up an x-ray interference pattern sensitive to any distortions in the x-rays due to the object, and detect those fine distortions. This raises for the first time the possibility of using phase contrast imaging in an operational setting. Our project seeks to investigate the application of gratings based phase contrast imaging to explosives detection using a combination of experimental and modeling tools.

Work during FYs 2007 and 2008 included setting up a phase contrast imaging testbed at the Henry Ford Health System in Detroit, MI. We acquired images, tested gratings fabrication techniques, and studied system performance. In FY 2007, we made initial progress setting up the testbed and acquiring images. Analysis software was written, and a theoretical investigation of possible system designs was completed. Work in FY 2008 focused on obtaining higher quality gratings, a challenging task given the small size and high aspect ratios needed. Several fabrication paths and designs were investigated. We eventually obtained gratings of sufficient quality that we were able to detect the presence of the x-ray interference pattern, which also allowed us to perform a preliminary study of the alignment sensitivity of the system. We found that most components of the system only weakly affect contrast. However, the instrument's signal to noise was insufficient for imaging.



Proof-of-principle phase contrast x-ray images of explosives simulants: a - optical image approximately two in across, b - absorption image, c - phase contrast image (vertical stripes are an artifact correctable with improved processing), and d - scatter image.

In FY 2009, we obtained yet another set of gratings that were fabricated using two different approaches. In combination with upgrades of both the detector and a translation stage, the signal to noise improved by an order of magnitude. With this increased signal, we were able to obtain phase contrast images, which were verified by observing that the relative contrast between different materials changed between the phase and absorption images. Due to small angle scatter, this technique also results in a third contrast mechanism.

We imaged several samples, including explosives simulants, composite materials, and biological materials. Clear differences between various contrast mechanisms were seen. Absorption images highlight higher atomic number materials such as metals. Phase images can indicate lower atomic number materials more strongly than absorption. The phase images also highlight edges and boundaries because the signal produced in phase contrast is proportional not directly to phase shift but to the local spatial derivative of the phase shift. Images suffer from phase wrapping artifacts; therefore, preliminary data processing approaches to remove these were investigated. Finally, the scatter images highlight small scale texture; materials such as powders or paper may appear strongly even when nearly invisible to other contrast mechanisms.

To the best of our knowledge, we are among the first few groups in the world to have an independent capability for this approach to phase contrast imaging. Because of the different information highlighted by each of the three contrast mechanisms, the technique shows great promise for providing enhanced information in an x-ray radiography measurement. This has the potential to improve detection algorithms and provide greater material specificity, a shortcoming of current x-ray measurements such as for baggage screening.

Spectroscopic X-ray Computed Tomography for Improved Explosives Detection

Timothy A. White, Erin A. Miller, Frédéric Noo (University of Utah)

◆ We are investigating a novel approach to computed tomography that will enhance the ability to identify materials. If successful, this technique has applications for homeland security (e.g., detection of explosives in baggage) as well as medical imaging (e.g., detection of plaque in cardiac vessels). ◆

X-ray computed tomography is a non-destructive evaluation tool that generates a three-dimensional image of the structure of an object and is used extensively in security screening for the examination of checked bags at the airport and as a medical diagnosis tool, commonly known as a CAT scan. In general, the information obtained in a computed tomography scan is proportional to a parameter of materials known as the linear attenuation coefficient, which is proportional to density and elemental composition—specifically, the effective atomic number, Z_{eff}. Some tomography systems use a geometry known as dual energy scanning, in which data are collected with information in two x-ray energy ranges or windows. This geometry allows better discrimination between density and Z_{eff} of a material and in turn enables better material identification. Our hypothesis is that using more energy windows will further enhance material identification and thus discrimination between benign and threat or disease materials; for instance, explosives in the case of security screening or plaque in the case of cardiac imaging.

However, full computed tomography scanning with an energy discriminating detector is not efficient with currently available electronics and detector materials. The principle constraint is that the required dynamic range, the range of x-ray intensities that must be detected, is too great when considering attenuation paths through both the center and edge of the object. If however we relax the dynamic range constraint by only considering the central (and highly attenuating) region of the object, we can develop a geometry and reconstruction algorithm to use the information from a detector with multiple energy windows. The geometry we have proposed is one that includes a detector of sufficient size but no energy discrimination for full computed tomography acquisition, and another smaller spectroscopic detector spatially limited to viewing only the central region of the object. The goals of the project are to determine if such a geometry can provide better material discrimination and to develop reconstruction algorithms to realize this advantage.

Accomplishments during FY 2009 included reestablishing our long-term collaboration with the University of Utah, refining a suite of forward projection and reconstruction tools developed over the course of that collaboration, defining critical early and long-term questions, and outlining early algorithm strategies. In a parallel effort, we acquired equipment necessary for experimental validation of our hypotheses through non-LDRD funds.

A critical question to be addressed is whether there is benefit to operating with multiple energy window data; i.e., whether we can show an improvement in material discrimination and whether we can develop an efficient algorithm for exploiting these data. We can address these issues with the simulation tools developed over the past decade. Simulation on noise free data will indicate the potential of the method and the addition of statistical noise will offer a step toward real world application. Another issue regarding practical implementation will be addressed if the initial analysis suggests a promising approach.

FY 2009 efforts were focused on identifying possible approaches, which are discussed below:

- If improved material separation with photon counting detectors can be achieved (as suggested in medical imaging literature for a full size detector), then we should achieve the same result for the interior problem with a smaller detector that is able to view only the central region of the object. An intriguing question, however, is whether the interior region of support can be increased in size with the additional information from a current integration detector.
- We will consider whether it is enough to determine whether there is some material (e.g., explosive) in the container without imaging. If we could map the attenuation coefficient accurately with a single pixel detector with higher spectral resolution, then we may be able to determine the presence of threat material without requiring imaging. Even if this is not a practical approach, the evaluation should provide an upper limit on the utility of spectroscopic capability.
- We may consider a primary/secondary interrogation scheme in which a very fast scan with the non spectroscopic detector defines a region of interest that could be interrogated with the spectroscopic detector.

In FY 2010, we expect to develop reconstruction algorithms for our proposed geometry. If our technique is mathematically tractable and/or shows improved materials discrimination, we will proceed with the experimental phase of the project.

Ultra-Pure Nuclear Physics Materials – Chemical Production of Copper

Eric W. Hoppe, Craig E. Aalseth, James E. Fast, Richard T. Kouzes

◆ This project will support the development of a research capability for ultra pure copper electroforming and will provide opportunities for further advances in materials science, allowing for the capability to determine the proper ties and purity needed for a range of future fundamental nuclear physics programs. ◆

Forefront research in neutrinoless double beta decay and dark matter rely on developing detectors with extremely low backgrounds from naturally occurring radioactivity in order to reach the desired sensitivities to observe these very rare processes. For example, the Majorana experimental goal is a background of only one event in a 4 keV region of interest around the neutrinoless double beta decay energy of 2039 keV per ton of active detector mass per year. This is a factor of 100, which is lower than previous generation experiments. It also represents an enormous challenge in the production and assay of materials used to construct and house the detector elements.

For several decades, PNNL and its collaborators have led worldwide efforts to achieve both the lowest measured radioactive backgrounds and the greatest discovery potential for new physics. In recent years, the driving force for this research has been a suite of national security projects that develop detectors for ultra low background counting. This work has moved the state-of-the-art forward by an order of magnitude in both material and surface purity as well as inductively coupled plasma mass spectroscopy assay sensitivity. Our project aims to support development of a research capability for ultra pure copper electroforming and will provide opportunities for further advances in material growth science, allowing for the capability to determine properties and purity needed for a range of future fundamental nuclear physics programs. The proposed work will draw on these advances and continue the research and development necessary to evolve these technologies and their application in order to meet the more stringent purity requirements of nuclear physics experiments in these areas.

During FY 2008, several important project features were completed, including the procurement (using non-LDRD funds) and initial setup of an electroanalytical system. New electronics for the PNNL ultra low background detector were also obtained. Further, construction and initial setup of a large scale electro forming apparatus was completed.

In FY 2009, a portable clean room necessary to perform work using ultra high purity materials was set up. The electroanalytical system was moved to the inside of a faraday cage, which was installed within the clean room. Installation of a large-scale electroforming apparatus into the portable clean room was also accomplished, including the multistep acid leaching processes to enable formation of ultra high purity material. Electroforming on a large scale stainless steel mandrel was begun in order to test scaling parameters from smaller-scale experiments conducted on the electroanalytical systems. By the second quarter of FY 2010, the growth of copper on the mandrel will be completed. At that time, the purity and physical properties of the material produced from the large-scale bath will be evaluated.

Among the several technical challenges of this project are determining rejection rates for various radioactive contaminants versus bath chemistry, current density, applied electric fields, and waveform at extremely low concentrations and determining ideal growth parameters to balance mechanical performance and growth rate against material purity. The research capabilities developed under this project will address significantly more challenging purity requirements, including unprecedented levels needed in both neutrinoless double beta decay and dark matter experiments. As previously stated, we anticipate from our project the development of a capability to produce ultra pure copper parts of the desired mechanical properties and radiological purity of interest to the Office of Science. Our results will enable the laboratory to build the necessary capabilities of interest to both the Majorana collaboration and the broader low background physics community. This project will be addressing much larger electroformed copper parts and much more stringent radiopurity requirements than prior work. Success in this critical area will extend our scientific leadership and visibility in the area of ultra low background technology and provide the technology necessary for the next generation of neutrino physics and dark matter experiments for the fundamental sciences community.

Appendix A

Fiscal Year 2009 Referred Publications

Appendix A

Fiscal Year 2009 Refereed Publications

During FY 2009, PNNL's LDRD Program resulted in 163 refereed publications. These journals articles, book chapters, and select conference papers are listed below in alphabetical order by the author's last name.

Aalseth CE, P Barbeau, DG Cerdeno, J Colaresi, JI Collar, P de Lurgio, G Drake, JE Fast, C Greenberg, TW Hossbach, JD Kephart, MG Marino, HS Miley, JL Orrell, D Reyna, RG Robertson, RL Talaga, O Tench, TD Van Wechel, JF Wilkerson, and KM Yocum. 2008. "Experimental Constraints on a Dark Matter Origin for the DAMA Annual Modulation Effect." *Physical Review Letters* 101(25), Article 251301.

Aalseth CE, JF Amsbaugh, FT Avignone, HO Back, A Barabash, P Barbeau, J Beene, M Bergevin, FE Bertrand, V Brudanin, W Bugg, T Burritt, YD Chan, JI Collar, RJ Cooper, R Creswick, PJ Doe, Y Efremenko, V Egorov, H Ejiri, SR Elliott, JH Ely, J Esterline, HA Farach, JE Fast, N Fields, P Finnerty, B Fujikawa, ES Fuller, V Gehman, GK Giovanetti, V Guiseppe, K Gusey, AL Hallin, R Hazama, R Henning, A Hime, EW Hoppe, TW Hossbach, MA Howe, RA Johnson, K Keeter, ME Keillor, C Keller, JD Kephart, M Kidd, O Kochetov, S Konovalov, RT Kouzes, KT Lesko, L Leviner, JC Loach, P Luke, S MacMullin, MG Marino, D Mei, HS Miley, M Miller, LK Mizouni, A Montoya, AW Myers, M Nomachi, B Odom, JL Orrell, AW Poon, G Prior, J Qian, DC Radford, K Rielage, RGH Robertson, L Rodriguez, KP Rykaczewski, AG Schubert, T Shima, M Shirchenko, J Strain, V Timkin, W Tornow, TD Van Wechel, I Vanyushin, K Vetter, RA Warner, JF Wilkerson, J Wouters, E Yakushev, A Young, CH Yu, V Yumatov, and C Zhang. 2009. "The Majorana Demonstrator: An R&D Project Towards a Tonne-Scale Germanium Neutrinoless Double-Beta Decay Search." In *American Institute of Physics Conference Proceedings*. PNNL-SA-67240, Pacific Northwest National Laboratory, Richland, WA. [Unpublished]

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Baldick R, B Chowdhury, I Dobson, ZY Dong, B Gou, DL Hawkins, Z Huang, M Joung, K Janghoon, D Kirschen, S Lee, F Li, J Li, Z Li, CC Liu, X Luo, L Mili, S Miller, M Nakayama, M Papic, R Podmore, J Rossmaier, KP Schneider, K Sun, D Wang, Z Wu, L Yao, P Zhang, W Zhang, and X Zhang. 2008. "Vulnerability Assessment for Cascading Failures in Electric Power Systems." In *Proceedings of IEEE PES Power and Energy Society Power Systems Conference and Exposition*. PNNL-SA-62287, Pacific Northwest National Laboratory, Richland, WA. [Unpublished]

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Appendix B

Fiscal Year 2009 Non-Referred Publications

Appendix B

Fiscal Year 2009 Non-Refereed Publications

In this appendix, 177 non-refereed publications or presentations resulting from PNNL's LDRD Program during FY 2009 are arranged in alphabetical order by the first author's last name.

2009. PNNL-18171 [Limited Distribution]

2009. PNNL-18631 [Limited Distribution]

Alexander ML, MK Newburn, A Mendoza, HW Kreuzer-Martin, RA Dagle, BR Johnson, and NL Canfield. 2008. "Aerosol Formation by Laser Ablation of Organic Solids for Stable Isotope Analysis Using a Miniature Flow Reactor." Presented by M Lizabeth Alexander at the American Association for Aerosol Research, Minneapolis, MN, October 27, 2008.

Anheier NC Jr. and BA Bushaw. 2009. "Isotope Enrichment Detection by Laser Ablation - Dual Tunable Diode Laser Absorption Spectrometry." In the Institute of Nuclear Materials Management Conference. INMM, Tucson, AZ.

Anheier NC Jr. and BA Bushaw. 2009. "Isotope Enrichment Detection by Laser Ablation Dual Tunable Diode Laser Absorption Spectrometry." Presented by Jon Phillips at the 50th Annual Institute of Nuclear Materials Management (INMM) Conference, Tucson, AZ, July 10, 2009.

Anheier NC Jr. and BA Bushaw. 2009. "Isotope Enrichment Detection by Laser Ablation, Absorption Ratio Spectrometry -- LAARS." Presented by Norm Anheier at the U.S. Department of Energy, National Nuclear Security Administration, Washington, D.C., September 23, 2009.

Arrigo LM, SA Bryan, R Christensen, M Douglas, DC Duckworth, CG Fraga, TG Levitskaia, M Liezers, CR Orton, SM Peper, and JM Schwantes. 2009. "Advanced Safeguards Technology Demonstration at Pacific Northwest National Laboratory." Presented by Leah Arrigo at the Institute of Nuclear Materials Management 50th Annual Meeting, Tucson, AZ, July 14, 2009.

Baer DR, AS Lea, CM Wang, and A Zelenyuk. 2009. "New Tools, New Knowledge: Enabling Innovative Environmental Research." Presented by Donald R Baer at the Electrochemical Society Meeting, Special Symposium: Role of Electrochemistry in Addressing Climate Change, San Francisco, CA, May 24, 2009 (invited).

Bailey VL, MI Boyanov, F De Carlo, N Fierer, M Hamady, R Knight, A Konopka, C Lauber, and LA McCue. 2008. "Fine-Scale Physical Structure and Microbial Composition of Soil Aggregates." Presented by Vanessa L Bailey at the American Geophysical Union Annual Meeting, San Francisco, CA, December 18, 2008 (invited).

Baker ES, EA Livesay, DJ Orton, WF Danielson, DC Prior, YM Ibrahim, RJ Moore, K Tang, RT Kelly, GA Anderson, ME Belov, and RD Smith. 2009. "High-Throughput, High-Sensitivity Proteomics Platform for Improved Biomarker Discovery and Verification." Presented by Erin S Baker at the CPTC 2009 Annual Meeting, Bethesda, MD, October 5, 2009.

Beagley N, C Scherrer, Y Shi, BH Clowers, WF Danielson, AR Shah, AM Mayampurath, GA Anderson, and RD Smith. 2009. "An Optimized Data Compression Strategy for Efficient Storage and Analysis for Multidimensional Separations and Mass Spectrometry." Presented by Nathaniel Beagley at the American Society for Mass Spectrometry, Philadelphia, PA, May 31, 2009.

Bellgraph BJ, GA McMichael, RA Buchanan, MC Richmond, KF Tiffan, WP Connor, and WA Perkins. 2009. "Juvenile Salmon Emigration Survival, Delay, and Associated Hydrodynamic Conditions in the Snake River Basin." Presented by Brian J Bellgraph at the American Fisheries Society Annual Meeting, Nashville, TN, August 30, 2009.

Bernacki BE, MC Phillips, and TA Blake. 2009. “Active Multispectral, Hyperspectral and Passive Hyperspectral Imaging of Explosives.” Presented by Bruce Bernackie at the DHS C-IED Lab Days, Washington, D.C., September 1, 2009 (invited).

Bishop M, C Gates, DA Frincke, and FL Greitzer. 2009. “AZALIA: An A to Z Assessment of the Likelihood of Insider Attack.” Presented by Matt Bishop at the 2009 IEEE International Conference on Technologies for Homeland Security, Waltham, MA, May 11, 2009.

Bond LJ, SR Doctor, JW Griffin, A Hull, and S Malik. 2009. “Damage Assessment Technologies for Prognostics and Proactive Management of Materials Degradation (PMMD).” Presented by Leonard J Bond at the 6th International Topical Meeting on Nuclear Plant Instrumentation Control and Human Machine Interface Technology, Knoxville, TN, April 8, 2009.

Bond LJ, SR Doctor, JW Griffin, A Hull, S Malik, and CEG Carpenter. 2009. “Damage Assessment Technologies for Prognostics and Proactive Management of Materials Degradation (PMMD).” Presented by Leonard J Bond at the American Nuclear Society 2009 Annual Meeting, Atlanta, GA, June 16, 2009.

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Buchko GW, WJ Shaw, K Mcateer, and RC Reeves. 2009. “Strategies for the NMR Chemical Shift Assignment of Intrinsically Disordered Proteins.” Presented by Garry W Buchko at the 2009 92nd Canadian Chemistry Conference, Hamilton, ON, Canada, May 31, 2009.

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Campbell LW, LE Smith, AC Misner, and JJ Ressler. 2009. “High-Energy Delayed Gamma Spectroscopy for Spent Nuclear Fuel Assay.” In Proceedings of the INMM 26th Annual Meeting. PNNL-SA-66814, Pacific Northwest National Laboratory, Richland, WA. [Unpublished]

Carson JP, AP Kuprat, X Jiao, F del Pin, and DR Einstein. 2009. “An Anisotropic Fluid-Solid Model of the Mouse Heart.” Presented by James Carson at Computers in Cardiology 2009, Salt Lake City, UT, September 16, 2009.

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Chen Y, S Jin, D Chavarría-Miranda, and Z Huang. 2009. “Application of Cray XMT for Power Grid Contingency Selection.” In Computer the Future, Cray User Group Meeting 2009. PNNL-SA-66173, Pacific Northwest National Laboratory, Richland, WA. [Unpublished]

Chen Y, S Jin, D Chavarría-Miranda, and Z Huang. 2009. “Application of Cray XMT for Power Grid Contingency.” Presented by Yousu Chen at Computer the Future, Cray User Group Meeting 2009, Atlanta, GA, May 5, 2009.

Choi D, D Wang, Z Nie, J Zhang, Z Yang, and J Liu. 2009. "Nanostructured LiMPO4 (M: Fe, Mn, Co) for Li-ion Cathode by Molten Surfactant Approach." Presented by Daiwon Choi at the 215th Electrochemical Society Meeting, San Francisco, CA, May 28, 2009.

Chowdhury SM, MU Mayer, X Du, L Shi, N Tolic, H Yoon, RJ Moore, AD Norbeck F Heffron, JN Adkins, and RD Smith. 2008. "Profiling Protein-Protein Interactions in Vivo by Cross-Linking and Mass Spectrometry." Presented by Saifaul M Chowdhury at the American Society for Mass Spectrometry and Allied Topics, Denver, CO, June 2, 2008 (invited).

Corley RA, KM Lee, AD Woodstock, KM Waters, GJM Webb-Robertson, NJ Karin, RC Zangar, JM Jacobs, and DJ Bigelow. 2009. "Center for Novel Biomarkers of Response (U54 ES016015) Project 2. Mouse Biomarkers for Chronic Inflammatory Stress-Discovery and Validation." Presented by Joel Pounds at the NIH Exposure Biology Meeting, Washington, D.C., January 13, 2009 (invited).

Cziczo DJ, O Stetzer, PJ DeMott, M Kamphus, J Curtis, S Mertes, O Mohler, and U Lohmann. 2008. "The Impact of Anthropogenic Lead on Atmospheric Ice Formation." Presented by Daniel Cziczo at the American Geophysical Union, San Francisco, CA, December 16, 2008.

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DuBois DL. 2009. "A Modular Approach to Catalysis of Multiproton and Multielectron Processes." Presented by Daniel L DuBois at UC San Diego, Department of Chemistry, San Diego, CA, December 4, 2009 (invited).

Ellis PD. 2009. "Investigating the Metal Binding Sites in Metalloproteins Utilizing Low Temperature Solid-State NMR Spectroscopy." Presented by Paul Ellis at the CryoNMR Symposium, Southampton, Denmark, on September 21, 2009.

Ewing RG and MJ Waltman. 2009. "Non-Radioactive Ionization Source for Selective Atmospheric Pressure Ionization of Explosive Compounds." Presented by Robert G Ewing at the Gordon Research Conference: Detecting Illicit Substances: Explosives & Drugs, Les Diablerets, Switzerland, June 17, 2009.

Fan J, JM Comstock, and M Ovtchinnikov. 2009. "Tropical Anvil Characteristics and Water Vapor of the Tropical Tropopause Layer (TTL): Impact of Homogeneous Freezing Parameterizations." Presented by Jiwen Fan at the ARM Cloud Modeling Working Group, Princeton, NJ, November 20, 2009.

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Farmer OT III, M Liezers, LMP Thomas, EW Hoppe, and HS Miley. 2009. "Micro-Becquerel/Kg of Th-232 in High Purity Copper Metal by ICP-MS." Presented by Tom Farmer at Methods and Applications of Radioanalytical Chemistry (MARC) VIII, Kona, HI, April 7, 2009.

Fast JD, WI Gustafson Jr., EG Chapman, GA Grell, SE Peckham, and R Schmitz. 2009. "Applying the Aerosol Modeling Testbed to Assess Modal and Sectional Predictions of Particulates and Aerosol Radiative Forcing Downwind of a Megacity." Presented by Jerome D Fast at the 11th Conference on Atmospheric Chemistry, 89th American Meteorological Society Annual Meeting, Phoenix, AZ, January 13, 2009.

Fast JD, WI Gustafson Jr., EG Chapman, RC Easter, and JP Rishel. 2009. "The Aerosol Modeling Testbed: A Community Tool to Objectively Evaluate Aerosol Process Modules." Presented by Jerome D Fast at the ARM Science Team Meeting, Louisville, KY, March 30, 2009.

Fast JD, WI Gustafson Jr., EG Chapman, RC Easter, and JP Rishel. 2009. “Using the 2006 MILAGRO Field Campaign as an Aerosol Modeling Testbed.” Presented by Jerome D Fast at the 2009 Annual Atmospheric Science Program (ASP) Science Team Meeting, Santa Fe, NM, February 25, 2009.

Felix EJ. 2008. “Active Storage.” Presented by Evan Felix at Seminar on Active Storage, online conference, November 6, 2008 (invited).

Fink GA and BJ Carpenter. 2007. “Visual Packet-Process Correlation for Computer Security.” Presented by Glenn Fink at the Canadian CVAC group visit to Pacific Northwest National Laboratory (PNNL), PNNL Richland campus, Richland, WA, April 4, 2007 (invited).

Fink GA. 2007. “Nontraditional Approaches to Information Security (Presentation to OSD).” Presented by Glenn Fink at Invited Brief to Dr. Charles Perkins, OSD, Washington, D.C., July 20, 2007 (invited).

Fink GA. 2009. “Cyber Analytics: Challenges and Solutions for Computer Security.” Presented by Glenn Fink at the SIAM Conference on Computational Science and Engineering, Miami, FL, March 2, 2009.

Ford JJ, JZ Hu, JA Sears, Jr., JH Kwak, and DW Hoyt. 2009. “Large Sample Volume, Constant Flow, High Temperature MAS Probe for Catalytic Systems.” Presented by Joseph Ford at ENC, Asilomar, CA, March 30, 2009.

Fulp EW, GA Fink, JN Haack, and WM Maiden. 2008. “Predicting Computer System Events Using Support Vector Machines.” Presented by Errin Fulp at USENIX LISA 2008, San Diego, CA, November 12, 2008.

Fulp EW, JN Haack, WM Maiden, and GA Fink. 2008. “Cooperative Infrastructure Defense.” Presented by Glenn Fink at the 2008 Workshop on Visualization for Security (VizSEC), Cambridge, MA, September 15, 2008.

Gao F. 2009. “Materials Behavior Under Extreme Conditions – Multiscale Computer Simulation.” Presented by Fei Gao at University Seminar at Washington State University, Pullman, WA, September 10, 2009 (invited).

Geffen CA, AH McMakin, and DJ Cziczo. 2008. “Transforming Our Ability to Predict Climate Change.” Presented by Charlette A. Geffen at AAAS, Boston, ME, February 16, 2008 (invited).

Gelston GM, KJ Castleton, BL Browne, RL Baddeley, KS Rohlfing, and JG April. 2009. “Techno-Social DSS for Container Inspection Operations and Critical Event Response.” In Systemics, Cybernetics and Informatics: WMSCI 2009. PNNL-SA-65156, Pacific Northwest National Laboratory, Richland, WA. [Unpublished]

Gelston GM, KJ Castleton, BL Browne, RL Baddeley, KS Rohlfing, and JG April. 2009. “Techno-Social DSS for Container Inspection Operations and Critical Event Response.” Presented by Gariann Gelston at the WMSCIP Conference, Orlando, FL, July 11, 2009 (invited).

Gelston GM. 2008. “PNNL's Common Operating and Response Environment (CORE).” Presented by Gariann Gelston at SRC Technologies, Richland, WA, September 23, 2008 (invited).

Gelston GM. 2009. “CORE Awareness Quad Chart.” Presented by Gariann Gelston at the July 28th DNDO/AMSC PRND Pilot FSE Mid Term Planning Conference, Seattle, WA, July 28, 2009 (invited).

Green MA, LM Arrigo, M Liezers, CR Orton, M Douglas, SM Peper, JM Schwantes, and DC Duckworth. 2009. “Electrochemically-Modulated Separations for Destructive and Nondestructive Analysis for Process Monitoring and Safeguards Measurements.” Presented by Michael Green at INMM 50th Annual Meeting, Tucson, AZ, July 16, 2009 (invited).

Green MA, LM Arrigo, M Liezers, CR Orton, M Douglas, SM Peper, JM Schwantes, and DC Duckworth. 2009. “Electrochemically-Modulated Separations for Destructive and Nondestructive Analysis for Process Monitoring and Safeguards Measurements.” In the INMM 50th Annual Meeting. PNNL-SA-66967, Pacific Northwest National Laboratory, Richland, WA. [Unpublished]

Greitzer FL and SL Clements. 2009. “Cyber Security Situational Awareness: Research Issues in Addressing Cyber Friendly Fire.” Presented by Frank L Greitzer at the Cyber Friendly Fire Avoidance Workshop, Colorado Springs, CO, February 4, 2009 (invited).

Greitzer FL, R Podmore, M Robinson, and P Ey. 2009. "Naturalistic Decision Making for Power System Operators." Presented by Frank L Greitzer at the 9th International Conference on Naturalistic Decision Making, London, United Kingdom, June 25, 2009.

Greitzer FL and JD Fluckinger. 2009. "Predicting Insider Threats." Presented by JD Fluckinger at the DoD Computer Network Defense Research and Technology Program Management Office Workshop, Linthicum, MD, June 22, 2009.

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Pacific Northwest
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U.S. DEPARTMENT OF
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Laboratory Directed Research & Development

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Pacific Northwest National Laboratory has an enduring mission to bring molecular and environmental sciences and engineering strengths to bear on DOE missions and national needs. Our vision is to be recognized worldwide and valued nationally for leadership in accelerating the rate of discovery and deployment of solutions to challenges in energy, national security, and the environment.