Laboratory Directed Research & Development

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

2008 ANNUAL REPORT

PNNL-18457

Laboratory Directed Research and Development Annual Report

Fiscal Year 2008

May 2009

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

Pacific Northwest National Laboratory
Richland, Washington 99352

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
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for the
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Laboratory Director's Message

At Pacific Northwest National Laboratory (PNNL), we deliver mission-critical research and development to secure America's future by providing the scientific and technical expertise to

- strengthen U.S. scientific foundations for innovation
- increase U.S. energy capacity and reduce dependence on imported oil
- prevent and counter terrorism and proliferation of weapons of mass destruction
- reduce environmental effects of human activity and create sustainable systems.

Our scientific discoveries and solutions are directly responsive to U.S. Department of Energy (DOE) and other agency objectives to conduct leading scientific research, expand and secure the nation's energy supplies, provide national and homeland security, and understand and manage the environment. Central to our ability to deliver these solutions is our internal investment in the development of new ideas and areas of expertise. We do this through our Laboratory Directed Research and Development (LDRD) program by funding a range of innovative ideas that can address current and projected national needs.

Strong and distinctive core capabilities are the enduring foundation of PNNL. Shaped by our history and past choices, our seven core capabilities are constantly renewed and refocused to position us for leadership in solving tomorrow's challenges. These capability areas[1] include the following:

- **Molecular Science and Engineering** includes capabilities in chemical physics, catalysis, geochemistry, analytical chemistry, and functional nanomaterials. This capability leads to new chemical signatures, improved energy conversion mechanisms, and enhanced understanding of geochemical processes. These capabilities have supported DOE's environmental mission and are expanding to include development of alternative energy sources with smaller carbon footprints.
- **Biological Systems Science** includes capabilities in environmental microbiology, applied proteomics, fungal biology, and predictive cellular, community, and system function. This capability enables new biosensors, bioconversion and bioremediation technologies, and biomarker discovery and validation. These capabilities have been essential to DOE's biological and environmental research mission and are currently being expanded and applied to developing biological processes for the conversion of biomass to high-value products.
- **Computational Science and Analytics** includes algorithms and software for the computational molecular, subsurface, and biological systems sciences as well as large-scale information analytics and data-intensive computing approaches and methods. This capability facilitates exascale simulation and knowledge discovery in key environmental, energy, and security applications. These capabilities have historically supported discovery science in biology, chemistry, and environmental remediation and are playing an increasingly important role in homeland and national security.
- **Earth Systems Science** includes capabilities in subsurface and atmospheric sciences, climate physics and regional climate modeling, and ecosystems science and integrated assessment. This capability supports global needs in understanding climate change, carbon sequestration, environmental remediation, water resource management, and energy facility licensing. These capabilities have supported DOE's missions in climate science and environmental remediation for several years and are used to address emerging challenges in climate change and carbon management.

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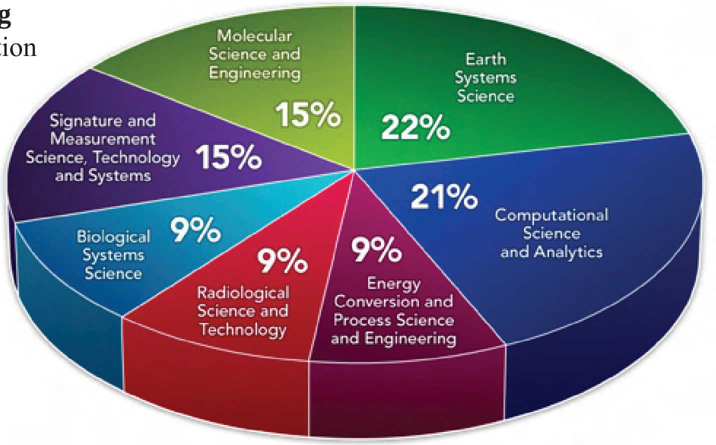
[1] PNNL's core capabilities have changed for FY 2010 and are noted in PNNL's Annual Laboratory Plan.

- **Energy Conversions and Process Science and Engineering** includes capabilities in advanced materials synthesis, separation and conversion processes, and engineered systems. This capability enables advancement in fuel cells, hydrogen storage, electrical energy storage, emission reduction, nuclear reactor life extension, advanced solid-state lighting, biomass conversion, and carbon capture and sequestration. These capabilities are being focused on national priorities for energy independence and security.
- **Radiological Science and Technology** includes capabilities in nuclear and radiochemistry, irradiated materials, surface and interfacial radiological science, and nuclear fuel cycle management. This capability enables new methods for radiation detection, nuclear explosion monitoring, forensics, and attribution, effluent analysis, and dosimetry. These capabilities have supported the Hanford Site operations and advanced nuclear fuel cycle research programs for more than 40 years. Over the last decade, national priorities focused on nuclear nonproliferation and counterterrorism have directed these capabilities toward the discovery, detection, and analysis of nuclear signatures and the control and detection of nuclear materials domestically and globally.



A view of how the PNNL's LDRD program supported the development of the Laboratory's seven capabilities in FY 2008.

- **Signature and Measurement Science and Technology** includes mass spectrometry, nuclear and infrared-optical spectroscopy, millimeter-wave imaging, selective separations and functional materials, high-resolution chromatography, discrete mathematics, statistics, and neutrino physics. This capability improves detection, characterization, and forensics technologies and is coupled with systems engineering and electronic systems expertise for development of robust measurement systems for demanding field applications. These capabilities have been historically applied to radiological and nuclear signatures and are expanding to encompass detection and characterization of the entire threat spectrum.

Recognizing the critical value of our LDRD research, we carefully conduct this DOE program in compliance with the objectives and guidelines outlined in DOE Order. 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 the Pacific Northwest National Laboratory Fiscal Year 2008 Laboratory Directed Research and Development Annual Report.

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) 2008.

Program Overview

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. 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.

The projects supported by LDRD funding are distributed across PNNL's major mission areas. All LDRD projects 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 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.

Individual project reports comprise the bulk of this LDRD report. 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 2009 should be regarded as progress reports; reports on projects completed in FY 2008 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 2009.

Mission Overview

As a DOE Office of Science (SC) national laboratory, PNNL has an enduring mission to deliver leadership and advancements in science, energy, national security, and the environment for the benefit of DOE and the nation. As an example of this leadership, PNNL operates 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 that comprised the Hanford Site research laboratories, PNNL continued its support of 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 that makes scientific discoveries and develops innovative technologies for DOE and other federal and industry customers. Today, the Laboratory provides science, technology, and leadership to increase U.S. energy capacity while reducing dependence on imported oil, prevent and counter terrorism and the proliferation of weapons of mass destruction, and reduce the environmental effects of human activity.

PNNL is operated by Battelle Memorial Institute (BMI), 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 2008 was $935 million. In addition to SC, principal PNNL customers include DOE's Offices of Energy Efficiency and Renewable Energy (EERE), Environmental Management (EM), Fossil Energy (FE), Electricity Delivery and Energy Reliability (OE), the National Nuclear Security Administration (NNSA), the Department of Homeland Security (DHS), Department of Defense (DoD), Nuclear Regulatory Commission (NRC), and National Institutes of Health (NIH).

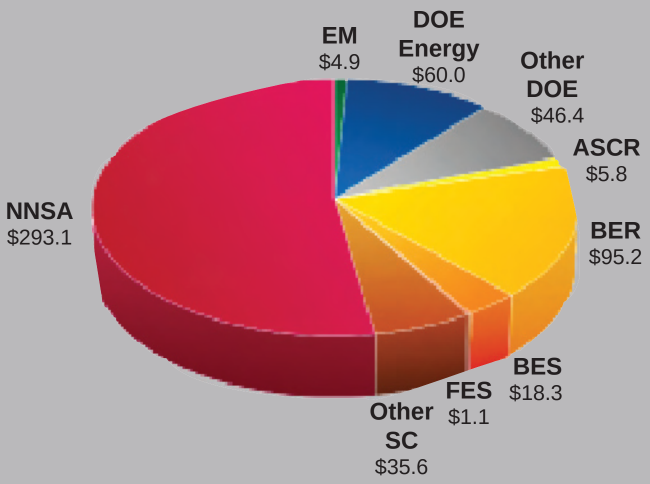
Laboratory at a Glance

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
- 1,968,000 gsf Total—715,000 DOE (224,000 SC, 491,000 EM); 390,000 BMI; 843,000 Leased and Other
- Replacement Plant Value: $104M (SC Only)
- Deferred Maintenance: $26K (SC Only)
- Asset Condition Index: 100%
- Mission Critical: 1.0 (Excellent)
- Mission Dependent: 1.0 (Excellent)
- Asset Utilization Index: 1.0 (Excellent)

Human Capital
- 3847 Employees
- 348 Students (not included under employees)
- 2515 Facility Users and Visiting Scientists

FY 2008 Total DOE Funding: $560.3M
FY 2008 WFO Funding: $145.6M
FY 2008 DHS Funding: $229.1M
Funding=Budget Authorization (BA)



FY 2008 DOE Funding (BA in millions).

Advanced Sensors and Instrumentation

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

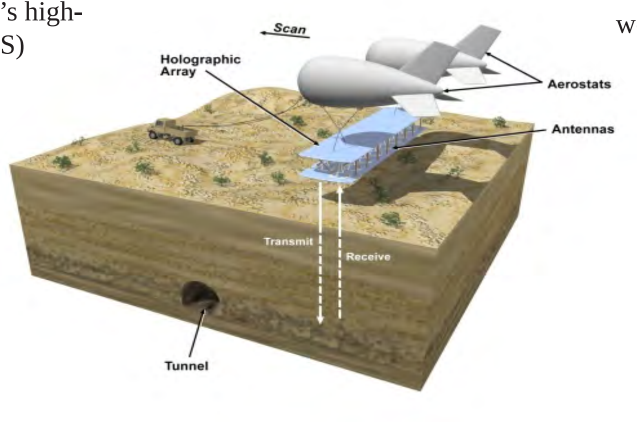
Douglas L. McMakin, Kyle J. Bunch, Gerald A. Sandness, Ronald H. Severtsen, David M. Sheen

◆ The objective 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 improvised explosive devices detection. ◆

Tunnels used by terrorists to smuggle weapons and other illicit materials across borders continue to be a security challenge for the military and law enforcement. In addition, improvised explosive devices are an ongoing concern to the military in Iraq and Afghanistan. To detect either of these threats, sensor technologies are required. Previously, ground-penetrating radar (GPR) systems have been used for these detection issues, but they are difficult to use on uncleared terrain. Additionally, conventional GPR systems perform optimally when they are in contact with the ground because it is much easier to couple the electromagnetic energy from the antennas to the soil that way. However, dragging a GPR system over the ground is a non-starter for improvised explosive device detection, and large-area tunnel detection surveys may be impractical if natural impediments such as heavy vegetation and large rocks or logs have to be removed.

We propose 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 improvised explosive device detection. 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. These antennas will be designed and modeled on PNNL's high-frequency structure simulator (HFSS) and fabricated and tested in combination with existing holographic radar transceivers.

Antennas used on GPR systems are typically linearly polarized, thereby limited in their 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 improvised explosive devices. 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.



Conceptual design of the holographic radar imaging tunnel and IED detection system.

This project has a dual purpose. For tunnel detection, the frequency of operation will be in the 50-300 MHz range; for improvised explosive devices detection, the operation will be 500 MHz to 2 GHz. As previously mentioned, a unique feature of the proposed system is that it can be mounted on a hover craft to survey large areas of terrain in near-real time. These antennas will be designed and modeled on Ansof's HFSS and then fabricated and tested in PNNL's Radar Imaging Laboratory. The transceiver, electronics, and holographic radar imaging algorithm have already been developed in previous projects.

We designed, modeled, and fabricated circular polarized antennas for improvised explosive device and tunnel detection on HFSS at 0.7-4.0 GHz using a spiral antenna design for improvised explosive device detection imaging and tunnel simulation imaging studies. We also designed, modeled, and fabricated 200-500 MHz spiral antennas for tunnel detection field prototype. We conducted holographic radar imaging studies using 0.7-4.0 GHz transceiver on improvised explosive devices/explosively formed penetrators and simulated tunnels at various depths in the test bed 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 GPR prototype imaging array.

Work planned for FY 2009 is to fabricate a field deployable holographic GPR imaging array operating at 200-500 MHz for preliminary ground penetrating imaging studies for tunnel detection.

Complex Adaptive Sensor Systems

Mary E. Peterson, Pamela M. Aker, Mitchell J. Myjak, Mark E. Jones

◆ Complex adaptive sensor systems developed under this project provide the ability to sense, measure, and detect objects in real time for emergency response, border security, coastal security, transportation security, inventory tracking, and materials protection, control, and accounting. ◆

For many broad homeland security applications, persistent monitoring systems are needed that can operate reliably with wide spatial coverage, with near constant sampling, and within an environment characterized by rapidly changing conditions. Complex adaptive sensor systems are particularly attractive because they can self-organize a network using onboard logic to interpret localized operating conditions and respond to triggers. Advances in processing speed, memory, and power savings will enable the sharing of higher bandwidth information. Location, routing, power usage, operations, and data format all can be used to configure the network for optimum data collection and transfer. Just as important, the network should be able to reconfigure itself on demand based on sensor response from individual or consolidated nodes.

During FY 2008, efforts were focused on improving communications between a sensor network and a central reporting location, and designing novel field programmable signal processors to analyze sensor response.

Frequency Modulated Free Space Optical Communications (FSOC). A new form of FSOC is being developed that is resistant to both atmospheric turbulence and atmospheric visibility changes. The specific objective is to demonstrate that frequency modulated spectroscopy can be used to transmit digital data over long distances of free space and to show that this type of optical communications is immune to atmospheric turbulence while reliably operating in severe weather. Our technology uses long-wave infrared light using a quantum cascade laser because this wavelength can penetrate mist, fog, and dust clouds.

Demonstration this past year that analog frequency modulated spectroscopy can be used to transmit digital data was an important achievement since it shows that the original hypothesis was correct. A digital FSOC system was built that is capable of sending data at a rate of 0.5 mega bits per second, five times faster than originally anticipated. The system had a measured bit error rate of 4.6×10^{-10} in a zero penalty environment, which represents a significant performance improvement over current commercial FSOC systems. Experiments show that the prototype bit error rate was limited in part by quantum cascade laser frequency instability and suboptimal electronic filtering that can be solved by incorporating a room temperature quantum cascade laser into the apparatus and changing two electronic components. A patent was submitted in January 2008 for the technology described here.

Additionally, a compact electronics package was designed and built that replaces multiple lab bench instruments were originally used to prove that frequency modulated absorption spectroscopy could be used to transmit digital data over free space. The electronics package, quantum cascade laser, telescope, and power supplies have been housed on a mobile optics bench that can be taken into the field and used for future client demonstrations. Because this type of optical communications is difficult to intercept, it is anticipated that the intelligence community will be interested in our technology. It is also expected that this technology will be of great interest to the commercial telecommunications industry.

Field Programmable Signal Processor. In the second year, the project initiated an effort to improve data acquisition by developing a signal processor based on a field programmable gate array (FPGA). The device will be able to process dozens of sensor channels simultaneously. It can easily be adapted to different types of detectors, will fit into the palm of a hand, and will greatly reduce the cost of commercially available systems. Physically, an FPGA contains a programmable array of logic cells, interconnection structures, and input/output modules. Current devices integrate special components within the array of cells, including memory units, communication modules, and even microprocessors that allow a single FPGA to implement a complete signal processing engine of 60 to 120 channels.

First-year accomplishments include developing a prototype of the processing circuit and completing initial verification of its performance. This effort was undertaken jointly with Washington State University, which developed an application specific integrated circuit applied as input for the programmable processor array. A MATLAB model of the data acquisition system has been developed in order to refine the algorithms used on the FPGA for data acquisition, which enables the user to study the effect of circuit noise and leakage current on the results.

In FY 2009, this project will complete two areas of development: the final prototype of the data acquisition system, and the software interface that will enable the system to be integrated easily into future projects. With this goal, the system will be tested in nuclear imaging and mass spectrometry applications, but new applications may arise through continuing dialogue with potential end users.

Development of a UF_6 Cylinder Integrated Portal Monitoring Capability

Karl Pitts, Michael M. Curtis, Eric Smith, Mark W. Shaver

◆ Non-destructive assay (NDA) verification on enrichment plant cylinders consists of monthly inspections at a large enrichment plant that takes two inspectors a number of days to complete. We propose the installation of a portal monitor at a key measurement point that will positively identify each cylinder, measure its mass and enrichment, store the data along with operator inputs in a secure database, and maintain the continuity of knowledge on measured cylinders until operator arrival. ◆

Enrichment plant interim safeguard inspections are time-consuming because inspectors spend the bulk of their time performing NDA measurements on UF_6 cylinders. All feed cylinders received and product and tails cylinders produced from the time of the last declaration (usually the day before the previous inspection) are considered flow cylinders for the current inspection. They are randomly sampled for NDA verification along with a much smaller sample of static inventory. PNNL wishes to automate cylinder verification activities to include measuring the weight, enrichment, and positively identifying each cylinder.

The PNNL portal monitor concept is based on large, inorganic NaI scintillators for gamma-ray spectroscopy. These detectors sacrifice the high resolution of a germanium detector for greater efficiency and significantly greater volume and stopping-power. Their low resolution makes them unsuitable for measuring the closely spaced energy lines associated with plutonium measurements, but their large volume allows for the detection of high-energy signatures. By measuring high-energy gammas, the PNNL portal concept can survey the entire volume (as opposed to the outer perimeter) of a cylinder. Finally, the monitor will measure neutron emissions, a signature ignored in present verifications. Taken together, the high-energy gamma-ray and neutron signatures should enable high-accuracy, high-precision estimates of the absolute ^{235}U mass in each cylinder.

During FY 2008, a team of PNNL staff members took a series of measurements at the AREVA NP Fuel Fabrication Facility with the following objectives:

- Estimate the variation in neutron and gamma-ray source terms for a wide-range of product cylinders to represent interfering background source terms.
- Collect detailed spectral measurements using high- and medium-resolution gamma-ray spectrometers of individual cylinders with well-known content in enrichment and mass. Measurements will be used to benchmark the PNNL-developed cylinder modeling framework.
- Identify high-energy gamma-ray signatures typically not considered in agency measurements but capable of being collected using large-volume NaI sensors with high-energy collection efficiency.

Detailed measurements were taken on a full Urenco cylinder containing non-recycled uranium, a Russian down-blended cylinder with recycled uranium, and an empty cylinder with heels. Background measurements were taken at two different locations with an Ortec Detective®, an Exploranium GR-135®, and a miniature version of the portal monitor enrichment panel containing three NaI detectors and eight moderated ^3He detectors.

Net neutron count rates indicate that the expected correlation with ^{234}U and ^{235}U mass may be realized. Neutron count rates were consistent in terms of proportionality to ^{235}U mass with a response of approximately 0.8 cps/kg ^{235}U. This measurement was performed in a configuration similar to what would be used in the UF_6 portal.

Gamma ray spectroscopy of these same cylinders using large-volume NaI spectrometers shows a relationship that corroborates the neutron analysis when correlating ^{235}U mass and high-energy count rates in the 4-7 MeV range.

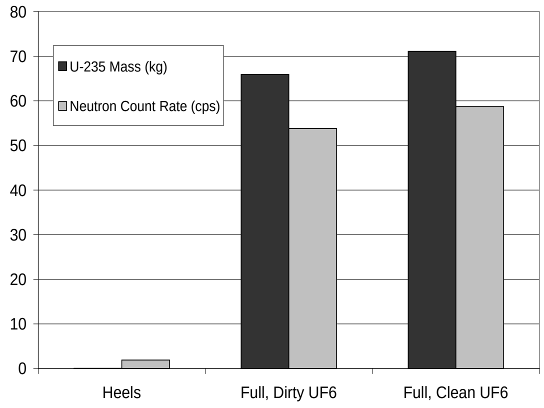
The AREVA measurements were invaluable for recording actual UF_6 cylinder neutron and gamma-ray signatures for benchmarking purposes, but the range of cylinder masses and enrichments was too narrow to support a more definitive analysis of the PNNL portal-monitor predicated performance. Validated by the AREVA measurements, modeling will be used to explore a broader cylinder parameter space and develop correlation and calibration curves that can support quantitative performance predictions.

Mass determination will be handled by commercial floor scale Mettler-Toledo Vertex with a capacity sufficient for weighing a full UF_6 product cylinder and the cart or

Measurement with NaI-^{3}He detector suite representative of portal monitor instrumentation.

sled it is riding on. Surveillance will be provided by the International Atomic Energy Agency's Next Generation Surveillance System, which will employ front-end motion detection, MPEG image compression, image authentication, and data encryption.

The portal monitor will employ some means of automated cylinder identification; options are still being investigated. One promising technique would employ the European Commission's Joint Research Centre *Laser Item Identification System*, which uses the intrinsic structure of the cylinder itself to provide identification. Laser scanners are used to build a database by recording the spatial irregularities and manufacturing defects of every cylinder within the operator's purview. Once a database is established, cylinders passing the portal scanner would be scanned and their features compared with every reference scan in the database to establish a match.



AREVA-NP measurements indicating correlation between neutron count rate and ^{235}*U mass.*

All operator inputs and portal monitor acquired information will be stored in a secure mailbox, whose system is shorthand for a computer network or other arrangement in which operators declare pertinent information regarding product cylinders as they are removed from the process area. Information is loaded to a system that prevents it from being altered at a later time. Upon passage of a cylinder, the operator might enter the cylinder number, tare weight (from the nameplate), declared gross weight, declared enrichment, and the date and time. The portal monitor would automatically add identification, measured gross weight, and measured enrichment.

Research conducted by PNNL in FY 2008 focused on the enrichment measurement process, since the remaining subsystems (with the exception of positive cylinder identification) consist of commercial off-the-shelf equipment that merely requires process integration to provide a systemic whole.

An enrichment modeling framework is being developed that will enable the rapid evaluation of instrumentation options and prediction of expected accuracy/precision performance for comparison to today's baseline methods. Cylinder measurements conducted thus far support this modeling framework. July field measurements of UF_6 cylinders have been shown to demonstrate how high-energy gamma-ray signatures and neutron signatures might be used in concert to achieve full-volume interrogation of cylinders. The analysis results garnered so far are encouraging. Preliminary analysis of neutron and high-energy gamma signatures indicate a strong correlation with the mass of ^{235}U in the cylinder as absolute mass, not just enrichment. Since the entire project depends on the viability of the enrichment measurement process, the goal is to establish firmly its efficacy in FY 2009.

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

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

◆ This project promotes national security efforts by exploiting variations in isotopic composition that can reflect regional geographic differences or differences in material processing techniques. The goal is to provide improved methods for precise, accurate oxygen isotopic compositions in nuclear materials and metal oxide surfaces. ◆

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. Regional differences in the isotopic composition of water are documented; such regional variations in oxygen isotope content are dependent on geographical latitude, elevation, and proximity to the ocean. Stable isotopes can also vary as a result of differences in industrial chemical processes. Oxygen isotopic composition has proven useful in the forensic analysis of a variety of materials because variations can reflect not only regional geographic differences but also differences in material processing techniques. Oxygen isotopic composition is a potential signature in nuclear forensic studies, but efforts to characterize ^{18}O ratios from strongly bound metal oxides with high precision and accuracy are complicated due to difficulty in quantitatively liberating oxygen from uranium oxides via combustion techniques.

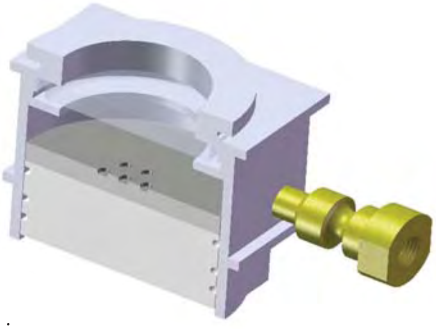
Chemical and physical processes (e.g., evaporation, condensation, isotope exchange) can fractionate stable oxygen isotopes (^{16}O, 99.762%, ^{17}O, 0.038%, and ^{18}O, 0.200%) in water. Because water is a common solvent for uranium processing and reprocessing, isotopic variations occur in actinide metal 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) has been successful in the analysis of oxygen isotopes and is proposed as a method of liberating oxygen from strongly bound metal oxides and for oxide-coated surfaces by high precision isotope ratio mass spectrometry. A laser fluorination interface for PNNL's dual inlet isotope ratio mass spectrometer will be developed to liberate and capture O_2 from UO_2 via laser-assisted reactions in the presence of BrF_5. LF-IRMS is the gold standard in oxygen isotopic analysis of various rocks and minerals due to the high precision (0.07-0.5/mil) and accuracy that can be obtained.

Due to the well-documented performance of LF-IRMS, the goal of this research is to construct a LF line to be interfaced with our dual inlet IRMS. 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, BrF_5). In the early 1990s, focused CO_2 laser (10 μm) heating was used to effect fluorination of refractory materials, allowing sample size requirements to be reduced from milligrams to sub-milligrams. The resulting reaction generates metal fluorides and O_2 gas that are collected for disposal and analysis, respectively. By defocusing the laser beam at a higher power, it may also be possible to sample larger surfaces, such as oxidized metal surfaces.

The primary FY 2008 accomplishment was to design and fabricate the laser fluorination line consisting of the laser desorption cell, gas manifold, and IRMS interface. This followed traditional designs of laser fluorination systems, but effort was made to reduce the fluorination line footprint for exhaust hood enclosure. Additionally, the laser desorption cell was designed and fabricated to allow both spot and defocused laser desorption for particle and surface sampling.

In FY 2009, testing of the laser fluorination IRMS system will continue, validating operations with standard reference materials. Optimization and characterization of the defocused laser technique will be conducted using silicon wafers, exposed to water vapor of differing oxygen isotopic compositions. Laser fluorination will permit oxygen isotopic measurements to be performed on metal oxides in support of nuclear forensic applications. Defocused beam laser fluorination will be used to extend the approach to surface oxides for forensic analysis of materials, including weapon components. This system will build PNNL's capability in the area of forensic signatures in the processing and reprocessing of nuclear materials.



Laser desorption cell allows both small sample and larger surfaces to be sampled. The cross sectional view shows the dimpled nickel sample support and the underlying Teflon spacer that accommodates solid samples of varying heights. Focused or defocused laser desorption occurs through the quartz window above the surface.

Enhanced Detection of Peroxide Based Explosives

David A. Atkinson, Robert G. Ewing

◆ Peroxide-based explosives have been identified in recent terrorist events around the globe. This project aims to provide the scientific basis for enhanced detection of these threat substances using currently deployed equipment that would provide a useful tool for homeland security and military missions where these materials may be encountered. This project has significant potential impact on U.S. national security by providing enhanced detection capabilities against an important type of emerging threat. ◆

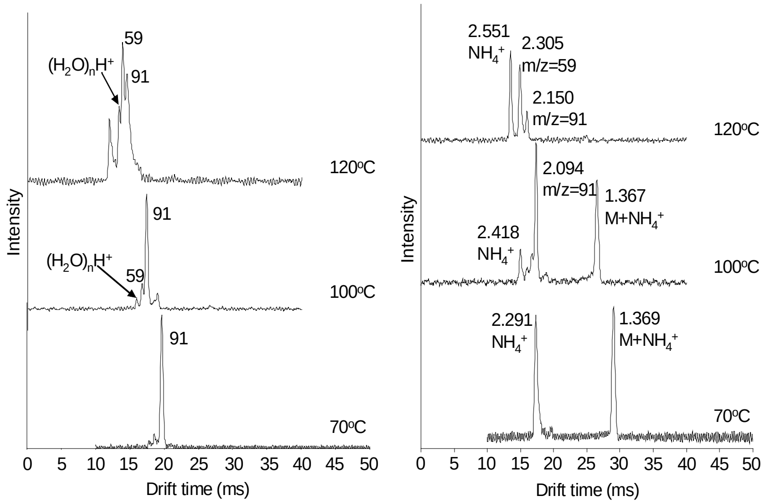
Terrorist attacks using explosives have become a daily event, and the effectiveness and impact of such attacks makes them a favorite tool of terrorists. This problem is further complicated by the emergence of new types of threats such as peroxide-based explosives, of which one of the most widely used is triacetone triperoxide (TATP), popular due to its ease of manufacture and the availability of starting materials. The goal of this project is to gain an understanding of the underlying science in fundamental gas phase ion chemistry as it relates to the detection of peroxide chemicals. This project investigates the adaptation of currently deployed trace detection equipment for the detection of peroxide-based explosives. It focuses on understanding the underlying ion-molecule reaction chemistry in ion mobility spectrometry (IMS) and manipulating it to provide a sensitive, selective detection solution that can be retrofitted to existing instrumentation.

IMS responses were investigated in detail for TATP under different temperature and reactant ion chemistries. IMS coupled with mass spectrometry was used to elucidate the details of IMS product ion formation; in addition, the reduced mobility values obtained for the various peaks were compared against literature values. The reduction of analyte molecules to fragments reduces the spectral uniqueness of the ion peak, thus reducing the confidence of detection. Peroxide chemicals are generally considered thermally unstable and are thus susceptible to detection degradation via fragmentation.

Molecular modeling was used to screen possible reactant ion chemistries that could provide not only an enhanced response but also potentially stabilize organic peroxide compounds such that they provide a molecular ion-based IMS response. Hyperchem is a computational chemistry package that uses molecular mechanics and dynamics as well as semi-empirical and ab initio calculations leading to structure and energy determinations of molecular ion clusters. The hyperchem results from various ion reactant chemistries were evaluated, and the ammonium ion was determined initially to provide the best theoretical basis for the formation of a stable ion-molecule cluster involving TATP. The computation modeling of potential reactant chemistries saved substantial time over screening candidates experimentally.

We next studied IMS response of TATP in the presence of ammonium ions at different drift tube temperatures and ammonia concentrations. Results showed the formation of a strong TATP cluster with an ammonium ion (as predicted computationally), which up to 100°C provided a strong unique IMS response. Above 100°C, the IMS signature degrades into fragments similar to those obtained with hydronium reactant ion chemistry. The hydronium-reactant ion chemistry shows fragment peaks only at all temperatures studied, where the ammonium reactant ion chemistry results in a strong TATP•NH_4^+ cluster below 100°C. This IMS peak was confirmed as the TATP•NH_4^+ by the mass spectrometer coupled to the IMS. It was also determined that there was optimal ammonia vapor concentration for TATP detection. Low concentrations provide ion chemistry similar to the hydronium ion, and at higher concentrations the ammonium adduct was dominant; however, when ammonia concentration increased further, a gas-phase rearrangement forming an imine was observed.

This project is aimed at applying and strengthening existing laboratory capabilities in trace detection, and will provide a greatly enhanced methodology based on the existing installed base of IMS explosives detection equipment, representing a much lower cost alternative than developing and deploying new instrumentation to detect peroxide based explosives. This sets the stage for the transition of breakthrough capability enhancements into existing and deployed systems.



Ion mobility spectra of TATP utilizing hydronium ion chemistry (left panel) and with ammonium chemistry (right panel) at differing temperatures.

Enhanced Isotope Ratio Measurement Capability

Helen W. Kreuzer, Robert A. Dagle, Bradley R. Johnson, Nathan L. Canfield, M. Lizabeth Alexander, Matt Newburn, Daniel J. Gaspar

◆ We propose to build a device that would interface with an existing isotope ratio mass spectrometer to permit oxygen and hydrogen stable isotope ratio analysis of samples 20-50 times smaller than can be measured with current technology. The ability to determine ratios of smaller samples is important for signature characterization of materials related to weapons of mass destruction, as well as the forensic analysis of such materials. ◆

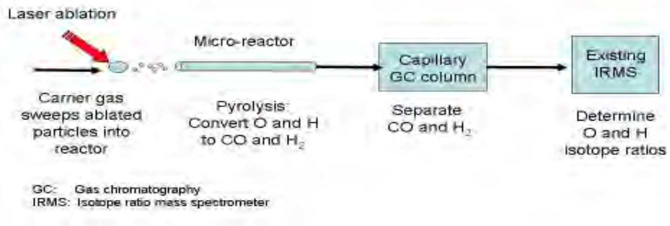
Chemically identical molecules can vary in their isotopic composition [e.g., the relative proportions of deuterium (^2H) and protium (^1H) they contain]; therefore, stable isotope ratios (e.g., $^2H/^1H$) of individual molecules and bulk materials can distinguish otherwise chemically identical samples. 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, stable isotope ratios of biological materials are a function of the nutrients, water sources, and growth environment of the organism from which 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.

The purpose of this project was to build a new microscale device to convert solid samples to gases so that oxygen and hydrogen isotope ratios can be determined using samples 20 to 50 times smaller than can be measured with current technology. Using a laser to chip off representative particles of the sample that can be swept into the micro-reactor in a carrier gas stream obviates the need for a sample container, enabling the use of a reactor with a small inner diameter. Within the reactor, particles will be pyrolyzed to convert the O and H atoms in the sample to CO and H_2 gas, which will then be separated in a capillary gas chromatography column. These product gases will be swept sequentially into an existing isotope ratio mass spectrometer (IRMS), where the oxygen and hydrogen stable isotopic content of the sample will be determined.

Demonstrated with both nylon polymer and horse hair, results showed that laser ablation products were the proper size to be transported in the gas stream, particles across the range of sizes produced had similar chemical composition, and no organic vapors were produced. We demonstrated complete pyrolysis of several liquid samples in straight capillary reactors coated with both graphite and BN.

In FY 2008, we used scanning electron microscopy to evaluate the performance of the two reactor coatings and found that the graphite displayed superior performance. With the demonstration of pyrolysis in the capillary reactor, this work was published in *Industrial Engineering Chemical Research*. A major effort during this year was 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 that the bond could survive heating and cooling without breaking. This problem was solved by development of a leak-tight pyrolysis temperature novel glass braze. The micro-channel reactor bonded with the new sealant leak-tight at 1400°C, and complete pyrolysis of butanol was demonstrated. An invention report has been filed describing this novel bonding material.

While the bonding technology was being developed for the microchannel reactor, the laser ablation system, capillary reactor, and capillary gas separation system were integrated with the IRMS. First, we determined that particles produced by laser ablation were converted to gases in the reactor. We successfully demonstrated that carbon monoxide produced from pyrolysis of laser-ablated sample products could be successfully captured and introduced into the IRMS for isotope ratio measurement. Thus, we were able to develop and integrate the technology as shown in the figure, making the isotope ratio measurement of small amounts of solid samples potentially feasible.



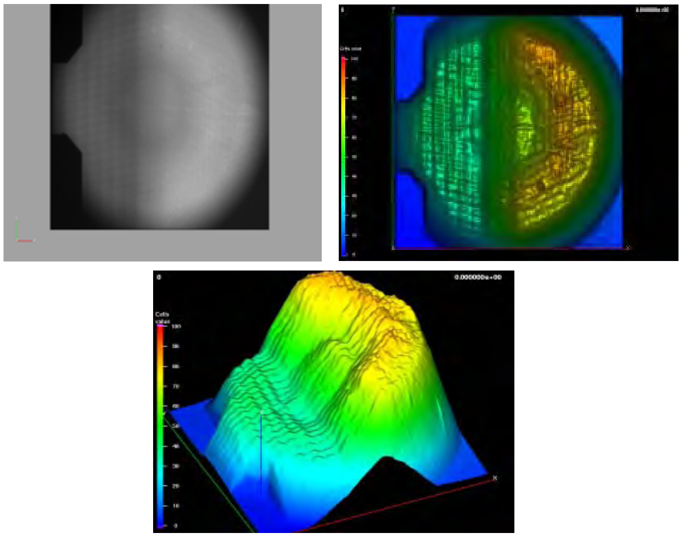
System design for oxygen and hydrogen stable isotope analysis of small samples.

Image Processing Methods Applied to the Detection of Highly Concealed Explosives

Harold E. Trease, Robert M. Farber, Duane L. Ward

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

The detection of highly concealed explosives will require a multi-sensor approach that includes spectrometers, chemical sniffers, biosensors, three-dimensional imaging devices, and object recognition image processing software systems. The use of non-intrusive sensors allows data to be gathered and processed in an automated manner, with the final step of the data analysis requiring a human being. A level of automation that integrates multiple sensor data requires that the data analysis be fast (in real and processing time) and accurate so that the chance of experiencing false positives and negatives is reduced through use of orthogonal and non-orthogonal sensors. The most accurate and robust detection option lies within the image-processing system that performs object recognition, clustering, classifying, and sorting. This level of processing will require sophisticated algorithms and high-performance capability.



The top left figure shows the raw grayscale phase contrast X-ray image. The top right image shows the shrinkwrapped image in a false color scheme, where the dominant wavelengths of the data become apparent. The bottom figure shows a three-dimensional projection of the middle image, where a height function is applied to the data to bring out the dominant wavelengths signals buried within the very noisy X-ray image.

The goal of this research is to produce a computational framework that supports the analysis of multi-sensor data to produce a probability-of-detection of highly concealed explosives. The outcome will be an image-processing framework that takes input from video, infrared, and millimeter (mm)-wave imaging systems in order to perform image segmentation, feature extraction and recognition and tagging/tracking that feed into clustering, classifying, and sorting algorithms that ultimately produce a probability-of-detection for detecting highly concealed explosives.

Progress made during FY 2008 involved a number of activities, including processing visible and infrared images/video and publishing our results. Our activities included the development and application of new image-processing algorithms using an image processing framework called Digital Data Analysis Tool Kit. This effort involved writing algorithms to transform mm-wave image data into facetted surfaces and tessellated volumes from which an isosurfacing algorithm extracts the external surface of the object. A shrinkwrap algorithm is used to collapse an ideal cylindrical surface using an average Laplacian-based algorithm onto this isosurface to obtain the final shrink-wrapped surface, which is a method for removing or concealing sensitive features (including high-frequency noise) in the original data. 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 mm-wave data into facetted surface and tessellated volume. We transformed ~150 three-dimensional point clouds representing the imaged people into a coherent facetted surface filled with a volume by using mesh generation algorithms NWGrid. The resulting surface/volume mesh was used to generate tables of area measures. Finally, we generated avatars representing generic people as surface and volume representations that may be used to get around privacy issues related to portal scanning devices, where the real surface of a person is replaced by that of a generic person not containing private parts. 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, Brian H. Clowers, Bill Danielson III, Brian L. Lamarche, Andrei V. Liyu, David C. Prior, Richard D. Smith

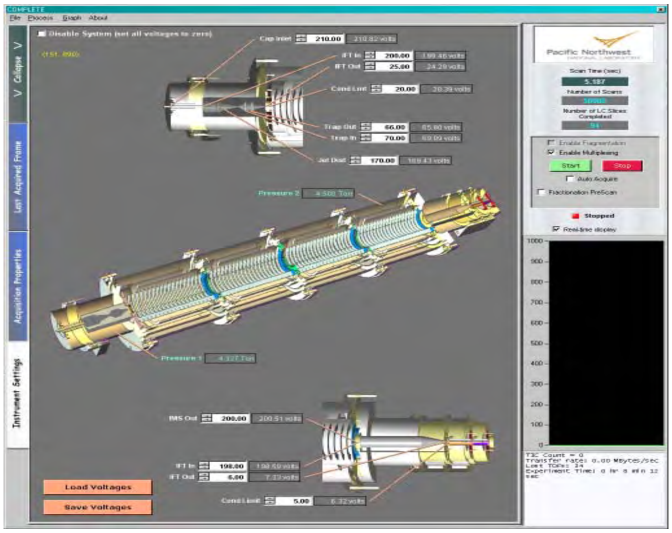
◆ Proteomics is rapidly becoming an essential tool for biological research, enabling new “systems biology” approaches for the discovery and validation of disease biomarkers and environmental perturbations. Enormous sample complexity and biological variability are best addressed with high-throughput,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

Over the past year, novel instrument control and data acquisition systems have been developed and fully integrated with the LC/IMS TOF-MS platform. Specific accomplishments are as follows:

- A novel data acquisition system (Acqiris, Geneva, Switzerland) has been designed. Compared with conventionally employed time-to-digital converters, the developed data acquisition system provides an order-of-magnitude greater dynamic range and up to 5-fold higher mass measurement accuracy. Both parameters are critically important in proteomics experiments with complex biological samples.
- State-of-the-art computer control of both components operated at a high voltage bias (“floating” components) and those referenced to the earth ground have been implemented. Instrument control of the platform floating elements is accomplished via fiber-optical couplers that ensure real-time uploading of complex experimental sequences into the analog and digital PCI cards. The latter determine the timing and potentials used to drive essential system components, including an ion funnel trap.
- A novel multiplexing approach has been developed and incorporated into the instrument control capabilities. Multiplexing implies introduction of multiple ion packets into an IMS drift tube on the time-scale of a single separation experiment results in up to 10-fold sensitivity improvement. A sophisticated algorithm for reconstruction of the encoded original data vector has been developed and integrated with the instrument control software.
- A novel approach for tandem MS experiments that makes the use of resonant dipolar excitation of ions assisted by additional radio-frequency heating has also been developed. The control electronics, segmented quadrupole hardware, and software tools have been incorporated into the IMS TOF-MS platform.

During FY 2009, emphasis will be on demonstrating robust, reproducible operation of the LC/IMS TOF-MS platform in high-throughput experiments with complex biological samples, enabling data-directed tandem MS experiments for improved identification of peptides from complex proteolytic digests, and developing of an intelligent auto-tune/-calibration procedure for the fully automated LC/IMS TOF-MS platform.



Cap Inlet 210.00
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Jet Dist 170.00
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IFT In 198.00
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Cond Limit 5.00
Scan Time (sec) 5.187
Number of LC Slices Completed 34

A snapshot of the LC-IMS-TOFMS instrument control software.

Laser Frequency Control for Trace Actinide Isotopic Analysis

Bruce A. Bushaw

◆ Diode laser-based ionization spectroscopy is being developed for the trace characterization of actinide element isotopic profiles. These measurements depend on the ultra-high resolution of single-mode continuous wave lasers to differentiate shifts in atomic transition frequencies for variable target isotopes. One of the challenges for routine analytical implementation is that three different lasers must be simultaneously tuned to exact photon energies with a relative precision of approximately one part in 10^9. This project is developing a system for the daily resetting of laser frequencies with this accuracy. ◆

The system for resetting laser frequencies accurately combines a commercial wavemeter with a scanning confocal Fabry-Perot interferometer (CFI) to allow the daily resetting of the absolute frequency of multiple (3) tunable single-mode lasers with a precision of one part in 10^9. This allows a priori tuning of the laser systems for ultra-trace analysis of actinide isotopes by triple-resonance auto-ionization spectrometry. Prior work was done by “tuning up” on the abundant and naturally occurring ^{238}U isotope and tuning relative laser frequencies to the minor isotopes (234,235,236) for isotopic profiling. This “tuning up” of three independent laser frequencies was time consuming and required considerable operator skill. The goal of this project was to provide a control system that could automatically reset laser frequencies on a daily basis once an initial optimization had been performed. System performance will be tested by comparing ionization signal intensity for ^{238}U using preset laser frequencies derived from the interferometric control system with that obtained from laser frequencies locally optimized for a maximum ionization signal.

Computer software was developed to measure the laser absolute frequency with the wavemeter and then interactively tune lasers to the coarse target wavelength with an optical frequency accuracy of ~30 MHz. This was implemented as a subroutine (WMSEEK) that could be incorporated into larger software systems used for controlling the three lasers during analytical measurements. The subroutine that we implemented and tested showed that lasers could be automatically tuned close enough to the desired atomic transitions to observe an ionization signal. A second existing subroutine (CENTER) then performed “intelligent” three-dimensional scanning of the laser frequencies to maximize the ionization signal and hence exactly center the three lasers’ frequencies on their respective atomic transitions.

Recently, a new subroutine (WMSTOR) has been developed that stores the laser characteristics at the optimized positions, including averaged (for precision) wavemeter readings, digital-to-analog converter values used to drive the laser frequencies to the optimized values, and interference fringe positions from the scanning CFI for each tunable laser relative to a reference fixed-frequency He:Ne laser. We upgraded the WMSEEK subroutine to use the values stored by WMSTOR to reestablish the exact same pattern of CFI interference fringes when the system is restarted. All of these were successfully implemented with the result that on initial startup, the laser systems automatically tuned to the exact resonance for excitation of a given reference isotope.

Tests showed that after an initial calibration with WMSTOR, the lasers could be reset to the correct frequencies over periods of weeks and would produce ionization efficiencies above 90% of that obtained by signal-based optimization. In fact, it was found that laser frequency re-setability was not the limiting factor in obtaining an optimized signal. Rather, other physical processes caused the long-term ~10% loss in efficiency, which included small Dopper shifts caused by changes in the sample atomization source pointing, Stark shift of the auto-ionization level by changing electric fields in the laser ionization region, and drifts in spatial overlap of the three laser beams. Nonetheless, an a priori unoptimized signal recovery of 90% is quite acceptable for routine analytical measurements. Further tests compared the capability for measuring isotope ratios starting with preset and optimized frequencies. Generally, there was no systematic bias in the determined ratios for ^{234}U, ^{235}U, and ^{236}U relative to ^{238}U; however, uncertainty increased slightly because of an increase in signal instability when the lasers are not tuned exactly to the atomic transition line centers.

The results of this work have led to the successful development of a system that has an increased capable of setting frequencies of tunable diode lasers with absolute precision. Prior to this research, one to two hours of tune-up by a skilled operator were required before analytical measurements could commence. The tune-up of laser frequencies is now automated and takes place in less than 30 seconds. Removal of these degrees of freedom also considerably simplifies other tune-up procedures such optimization of ion optics and laser spatial overlap. We are now using the system for measuring uranium isotope ratios in real unknown samples and complex matrices.

Metal Beta-Diketonate Polymers for Selective Concentration of Explosives

Scott D. Harvey, David W. Koppenaal, Robert G. Ewing, Thomas J. Wenzel

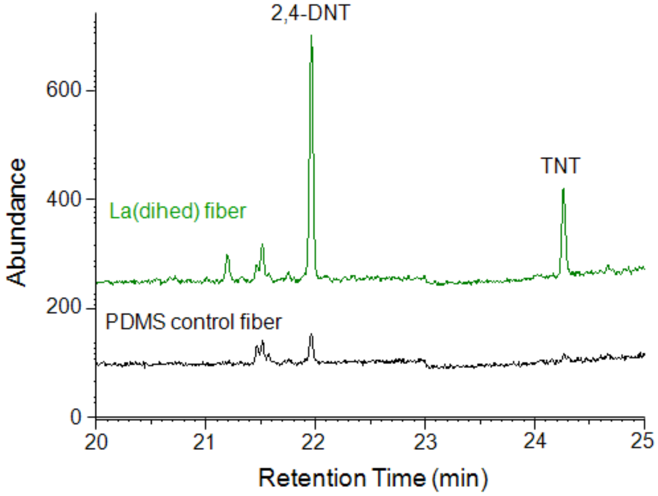
◆ This project investigates the ability of metal β-diketonate polymers to concentrate explosives selectively, resulting in a relatively pure and concentrated fraction for further analysis. Due to the simplified composition of the initial fraction, streamlined field-portable instrumentation that operates at high levels of performance can be designed to accomplish trace gas-phase explosives analysis. ◆

Previous researchers described selective capture of alcohols and amines (Lewis base analytes) on metal β-diketonate polymers (Lewis acidic polymers) from complex samples such as urine, cologne, and cigarette smoke. This project investigates the gas-phase interactions of metal β-diketonate polymers with explosives. Although not previously studied, interactions between metal β-diketonate polymers and explosives might be expected based on the basicity of the nitro group. Chromatographic studies quantitatively investigated the polymer/explosive interaction strength (as defined by the capacity factor) as well as the selectivity (ability to discriminate against the matrix background interferences) as indicated by the Kováts index. Once preliminary experiments were conducted, metal β-diketonate polymers were incorporated into advanced analytical formats and evaluated for the ability to capture selectively trace-level explosives under realistic conditions.

A variety of metal β-diketonate polymers were synthesized and assessed for their gas-phase interaction with nitroaromatic, nitrate ester, and peroxide explosives using packed column gas chromatography. The La(III) complex of *p*-di(4,4,5,5,6,6,6-heptafluoro-1,3-hexanedionyl)benzene [La(dihed)] showed 13 to 42 times the retention for the nitroaromatics compared to a control column (identical column but lacking the 5% loading of the metal β-diketonate polymer). Nitrate esters, the peroxide explosive triacetone triperoxide, and a dinitroalkane taggant were too strongly retained to elute from the La(dihed) column; however, these compounds could be eluted from the less retentive Cu(dihed) or Zn(dihed) columns. A Kováts index of 2124 for 2,4,6-trinitrotoluene (TNT) on the La(dihed) column compared to 1662 on the control indicated discrimination against nonpolar hydrocarbons, the principal matrix interference expected in air samples. A proof-of-principle experiment demonstrated analysis of an extrapolated 47 parts-per-trillion (ppt, v/v) of TNT in an air extract concentrate.

Further studies focused on solid-phase microextraction (SPME) using β-diketonate polymers. La(dihed)-coated SPME fibers were evaluated under realistic conditions by sampling the air within a Conex container that was used as an explosives bunker. TNT concentration in the bunker air was estimated at less than 3 ppt (v/v). Analysis demonstrated an approximate 10-fold enhancement in the quantity of 2,4-dinitrotoluene captured on the La(dihed) over the polydimethylsiloxane (PDMS) control fiber. La(dihed) sampling also resulted in a strong signal for TNT, whereas this explosive was not visible in the chromatographic trace from the PDMS control. These results are highly significant, since PDMS fibers (used as controls in this experiment) are often used for trace analysis and are relevant because the experiment closely parallels the challenging task of detecting hidden explosives in cargo containers.

Metal β-diketonate polymers interact strongly with a variety of explosive types. The ability to discriminate against matrix background hydrocarbons was quantitatively demonstrated using Kováts index studies as well a proof-of-principle experiment that analyzed an extrapolated 47-ppt TNT (v/v) in a complex air extract concentrate. Subsequent SPME experiments using a La(dihed)-coated fiber demonstrated ultra-trace analysis of TNT (more than 3-ppt, v/v) in a Conex container, an analysis that could not be accomplished by traditional nonselective PDMS SPME sampling, thereby demonstrating the feasibility of selective high-affinity capture on La(dihed) for detecting hidden explosives in cargo holds. Additional advanced analytical formats will be pursued in FY 2009 with an emphasis on field portability.



Analysis of SPME fibers used for sampling air in a Conex container by gas chromatography/mass spectrometry with selected ion monitoring. The vapor-phase concentration of TNT in the room was estimated at less than 3 ppt (v/v). Enhanced capture was evident with the La(dihed) fiber collecting nine times more 2,4-DNT than the control, giving a strong indication for TNT that was absent from the control.

Real-Time Electrical Resistivity Tomography System for High Resolution Environmental Characterization

Christopher E. Strickland, Kathryn E. Draper, Anderson L. Ward

◆ This project will develop a novel geophysical system for rapid subsurface change detection monitoring and characterization. Innovative methods will be applied to electrical resistivity tomography design to enhance temporal and spatial resolution to levels that are currently unattainable even with high-cost custom equipment. This will allow rapid monitoring of a range of processes from waste retrievals to the injection of reactants and even the effects of rapidly fluctuating river stage on groundwater and contaminant movement with the added benefit of being able to make real-time management decisions. ◆

Electrical resistivity measurements can provide images of the subsurface environment and processes, but data collection to support real-time decision making is hampered by hardware limitations. At present, electrical resistivity systems are also limited by the practical number of electrodes and the speed at which measurements can be acquired. Better spatial resolution can be gained by decreasing electrode spacing, but this increases the number of electrodes and data acquisition time, thereby hampering the ability to detect changes and make decisions in real time. Typical commercially available instruments produce current at two locations and detect the electrical potential generated at one or a limited number of adjacent locations. The concept of the system described is simply to parallelize the data acquisition by simultaneously measuring the potential generated at all points.

In addition to increasing the number of potentially synchronized measurements, significant improvements can be made by simultaneously introducing current at multiple electrode locations. This capability allows for substantially higher acquisition rates and larger signal-to-noise ratios. Software for processing configurations involving multiple current sources does not currently exist. In order to deliver physically based resistivity images, three-dimensional inversion of datasets containing multiple simultaneous transmitters must be performed.

Hardware integration of three components needed to construct the electrical resistivity tomography system was essential. This task was completed along parallel architectures, each using different data acquisition systems, which served as the control unit to provide an interface to either a Zonge ZT-30 or California Instruments AMX-112 and an array of CSI SDM-16AC relay multiplexers that provide a means to select electrode configurations. The ZT-30 is a 400-volt power transmitter capable of providing both time- and frequency-domain pulsed signal sources. The objective was to construct a system that could span the full range of resistivity measurements from DC through high frequency spectral. Both of these devices require serial commands for their operation, which are provided by the data acquisition system.

A two-dimensional flow cell was constructed to test the new electrical resistivity system. Numerous ground reference electrode configurations were tested to determine optimal cell design. The flow cell was packed several times, with a homogeneous synthetic material for initial electrode configuration followed by subsequent heterogeneous packs. Measurement signal and background noise were assessed for each electrode configuration and directly compared with two commercial electrical resistivity tomography systems. Potential measurements using dipoles comprised of spatially adjacent electrodes were least susceptible to noise and able to observe sufficient signal. The use of separate current and potential conductors greatly reduced inductive effects from the transmitter that can corrupt potential measurements. Using a complete set of measurements from 45 electrodes, our system was able to complete data acquisition 32.4 min compared with 991.2 min for a single channel commercial system. During this stage, a novel electrode configuration was tested that allows for substantially higher acquisition rates and larger signal-to-noise ratios. To our knowledge, this is the only such system in existence.

In FY 2009, it is planned that software will be developed to invert three-dimensional datasets containing information from multiple simultaneous transmitters. The current electrical resistivity system is capable of monitoring 20-volt peak-to-peak power output, which is sufficient for laboratory analysis. The new electrical resistivity system will be configured and tested for field settings to confirm that improvements observed in laboratory tests are realized in the field. The end goal is development of an ultra-fast electrical resistivity tomography system that will demonstrate real-time subsurface testing. As deep vadose zone remediation strategies such as desiccation, pump and treat, and reactive barrier injections drastically alter subsurface properties, real-time resistivity monitoring can detect such changes and provide high-resolution temporal and spatial imaging.

Real-Time In Situ Millimeter Wave Sensors for Gasifiers

S. K. Sundaram, John S. Mccloy, Jarrod V. Crum, P. P. Woskov (PSFC, MIT)

◆ Conversion of coal into clean-burning liquid fuel shows significant promise from economic, environmental, and security perspectives. This research supports DOE's mission areas of increasing conservation and energy efficiency while developing new energy sources. ◆

With high crude oil prices, conversion of coal into clean-burning liquid fuel offers an economic, environmental, and security solution. For several reasons, these 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 physical measurements, but sensors based on new technologies need to be developed in the next 5 years, tested in situ in operating plants, and demonstrated in a "smart plant" in the next 10 to 15 years. Most power plants are not equipped with state-of-the-art sensing capability, and sensors are not currently available to meet Vision 21 plant needs.

Millimeter wave (MMW) of electromagnetic radiation in the 30- to 1000-GHz range is ideally suited for remote measurements in the harsh environments of gasifiers. MMWs are long enough to penetrate optical/infrared obscured viewing paths through dust, smoke, and debris commonly encountered in gasifier environment but short enough to provide spatially resolved point measurements for profile information. Another important advantage is the ability to fabricate efficient MMW gasifier viewing components from refractory materials. Some refractories and alloys can be used to fabricate MMW wave-guide/mirror components. We propose to build on this technology to develop a remote sensor system for several parameters important to the efficient and cost-effective operation of gasifiers.

The specific objectives of this project are to use existing millimeter wave sensor technology to measure gasifier temperature, slag viscosity, and refractory corrosion; demonstrate proof-of-principle parameter measurements; design, build, and test an integrated prototype to measure parameters; and demonstrate sensor technology in a gasifier testing facility.

Since FY 2006, we made significant progress on every aspect of the project. Select results are summarized:

- We established and tested a dual-receiver MMW diagnostics system (custom-built in collaboration with MIT) for high-temperature measurements in simulated gasifier environments in the laboratory as well as in a research gasifier.
- We measured the MMW emission of three industrial slags and three refractory samples of interest to U.S. coal industries at 137 GHz as a function of temperature from room temperature to 1550°C. Refractories and slags are transparent for passive/active sensing modes of operation at high temperatures. As a result, we can differentiate refractories and slags. The samples show high emissivity (about 0.7) with distinct temperature dependence.

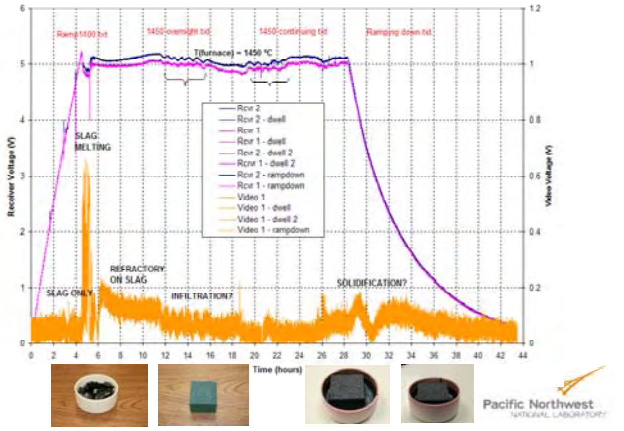
In FY 2008, we completed the following proof-of-principle tests:

1. Slag penetration into the refractory
2. Viscous flow of the viscosity standard fluids along the alumina slab at room temperature
3. Viscous flow of the viscosity of slag along the refractory wall at higher temperature.

- The MMW system was interfaced with a novel research gasifier assembled at PNNL using a flange system. The gasifier will be operated at ambient and higher pressures. In case of high pressure operation, an isolating flange system was used for interfacing with the MMW system.
- A poster presentation was made at an international conference, and one presentation was at the Pittsburgh Coal Conference.

During FY 2009, we will complete proof-of-principle measurements on slag flow and slag penetration into the refractory. We will plan and design demonstration of the MMW sensor capability using the research gasifier assembled at PNNL.

Overview of Slag Infiltration Test



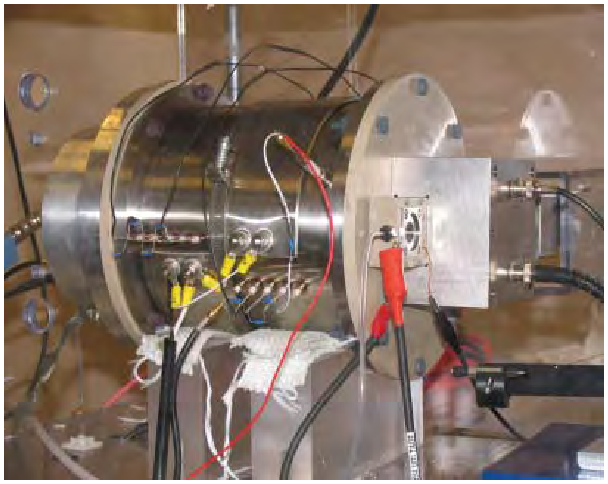
Sensitive and Specific Detection of Explosives Using a Multiplexed Two-Dimensional Field Asymmetric Waveform Ion Mobility Spectrometry/Ion Mobility Spectrometry (FAIMS/IMS) System

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

◆ This project will create a new 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. The system is envisioned to screen for explosives in the "sensitive" mode and, in case of a presumed detection, switch to the "specific" mode, employing FAIMS/IMS for confirmed identification. ◆

Present IMS systems for explosive 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 explosive 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 quite common.

This research will result in the first IMS system for explosives detection using effective ion packet multiplexing. The second outcome will be a portable two-dimensional FAIMS/multiplexed IMS capability (operating at ambient conditions) that will increase the explosive detection specificity by at least 10 with sensitivity equal to that of current IMS. Finally, we will characterize the performance of those new IMS-based technologies for explosive detection, including mapping separation parameters for common explosive substances and matrix interferences in the FAIMS/IMS space.



High-resolution FAIMS/IMS system that allows drift tube heating.

In FY 2008, our main focus was on completing construction of new FAIMS/IMS system (see figure) and its testing. Once the hardware assembly was finalized, the project satisfied PNNL safety regulations regarding the enclosure and warning signals. The custom operating software was coded, tested, and is fully debugged. The instrument was evaluated using both ESI and corona discharge sources with good sensitivity obtained in both cases. The ion filtering in CV dimension has been demonstrated by scanning the FAIMS stage and monitoring the signal at IMS detector.

We have struggled to obtain the expected IMS resolving power (R) of ~100, however. Maximum R achieved thus far was ~20, but even that level created minimum gate opening times and thus a low duty cycle. Suspecting improper gate functioning, we have replaced the original homemade Tyndall gate (with 1-mm gap) by a commercial product with a 0.5-mm gap and a gate with the same gap sold specifically for IMS use. Another probable cause of poor resolution is ion clustering with impurities in the N_2 drift gas that even in minute amounts become critical at ambient pressure. This issue can be solved by filtering the incoming gas to remove impurities and/or heating the IMS drift tube to prevent their condensation on ions. To implement the first, we have procured parts and are setting up gas filtering units, employing molecular sieves. Additionally, we installed resistive heaters and thermocouples for temperature control. To permit heating to ~200°C, we modified the drift tube by removing all plastic parts, installing thermal shielding, and moving the voltage divider outside the tube. Thus, a heated drift tube with various gating options is ready for evaluation that will commence in FY 2009.

In parallel with the troubleshooting of ambient-pressure FAIMS/IMS platform, we have explored options to improve FAIMS specificity via control of asymmetric waveforms. Previously, the rectangular profile with 2:1 high/low amplitude ratio was believed to provide best resolution. That derivation ignored the non-quadratic terms of $K(E/N)$ expansion underlying FAIMS separation, which was reasonable for early systems operated at relatively low E/N ~60 Td but not modern units using over 90 Td. Global waveform optimization has revealed that higher $K(E/N)$ terms affect the best waveform profile. The optimum profiles for ions that are "type B" in the relevant E/N range (including typical explosive traces) substantially differ from those used in current FAIMS systems and should improve the resolution by up to two times.

Sensor Platforms for Biomarkers of Response to Biological Agents – Immuno-PCR Bead Assays for Detecting Early Biomarkers

Susan M. Varnum, Marvin G. Warner, Richard M. Ozanich, Heather Edberg,
Yuehe Lin, Cynthia J. Bruckner-Lea

◆ Exposure of a population to a biological weapon agent requires the development of sensitive, easy-to-use, portable biosensors capable of the rapid specific detection of various bioweapon agents. This project will lead to the development of an immuno-PCR bead assay that will have the required sensitivity to detect host immune responses to biological weapon agents from readily accessible bodily fluids such as saliva. ◆

There is an urgent need for rapid, highly sensitive, specific, easy-to-use diagnostics to identify individuals exposed to Category A, B, or C pathogens. Traditionally, the clinical sample of choice to screen exposed individuals has been serum. However, when screening either large or field populations, saliva samples offer an attractive non-invasive alternative to blood testing. In general, saliva biomarkers are present at a greatly reduced concentration compared with serum, requiring assays with increased sensitivity.

This project addresses the need for more sensitive diagnostic assays for the detection of bioweapon agents, with an initial focus on the detection of the host immune response to *Francisella tularensis*, the highly infectious causative agent of tularemia that requires the inhalation of as few as 10 organisms to result in disease. For this reason and the ease of its dissemination, the Centers for Disease Control and Prevention lists *F. tularensis* as a Category A pathogen.

In order to identify protein biomarkers in saliva or serum from individuals exposed to Francisella, an ultra-sensitive assay is essential, requiring both sample concentration and purification, as well as signal amplification. Sample concentration and purification require the use of a selective affinity reagent to the antigen of interest. Antibodies provide the highest specificity affinity interaction with protein antigens, and the selective nature of antibody binding allows the use of these reagents in the development of methods that are not only highly specific but can also be used in complex biological fluids such as serum, urine, or saliva.

Our immuno-PCR approach combines the use of antibodies for sample concentration and purification with a PCR step for signal amplification. We will use magnetic microbeads (MMPs) coupled to antibodies specific to the protein of interest, allowing for the concentration and purification of biomarkers from clinical fluids onto magnetic beads. Next, the MMP-antigen complex is incubated with gold nanoparticles (NP) conjugated with both specific antibody and hundreds of short DNA molecules. The DNA oligonucleotides provide two types of signal detection; alternatively, the oligonucleo-tides will be amplified using PCR methodologies, providing a powerful signal amplification. This strategy will enable the ultratrace detection of biomarkers in complex biological fluids.

Results from experiments performed in FY 2006 demonstrated the detection of IL-8 in buffer, serum, and saliva using an immuno-PCR bead assay with a sensitivity of ~100 pg/mL. In FY 2007, the assay was re-designed using improved magnetic beads and conjugation protocols in an effort to develop reagents with decreased non-specific binding, thus providing better signal to noise ratios. Additionally, because of the change in focus within the RBA focus area, the assay was developed for the detection of TNF α, a cytokine that increases in the host in response to infection with *F. tularensis*.

Following generation of reagents for the detection of TNF α, the immuno-PCR assay was used to measure TNF α in buffer with a lower limit of detection of 0.1 pg/mL. The assay has also been tested in both plasma and saliva with slightly higher limits of detection of 1 pg/mL. This sensitivity represents a 10-fold improvement over other antibody-based detection methods. However, it is expected that the use of nucleic acid amplification detection will result in even lower levels of sensitivity. Therefore, further experiments were initiated to increase the signal to noise ratio, including optimizing the blocking and washing conditions of the assay. Additionally, the assay was re-designed using reagents with improved stability and specificity and relying on the formation of a sandwich complex consisting of a specific antibody conjugated to magnetic microparticles, the antigen, and antigen specific antibodies conjugated to biotin. Following these steps, the complex was incubated with streptavidin conjugated nanoparticles and finally biotinylated oligonucleotides, the latter of which were utilized for the nucleic acid amplification step to provide ultrasensitive detection of the antigen. The re-designed assay was tested; however, no additional benefits were seen. The sensitivity of the assay is 0.1 pg/mL in buffer and 1 pg/mL in plasma and saliva. We expected an improvement in the stability of the nanoparticle and microparticle reagents; however, the reagents continued to have limited storage of approximately one month. Until reagent stability is successfully resolved, this assay has limited applicability.

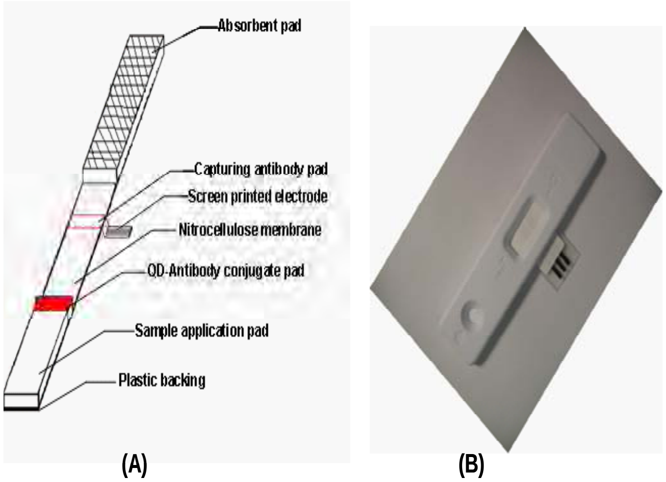
Sensor Platforms for Biomarkers of Response to Biological Agents – Nanoparticle Immunoassays for Detecting Protein Biomarkers

Yuehe Lin, Jun Wang, Hong Wu, Susan M. Varnum

◆ This project will develop a nanoparticle label and electrochemical immunoassay platform for the detection of protein biomarker response to biological agents. The new bioassay platform will be more portable, sensitive, selective, and supportive of real-time needs than conventional methods that require large fluorescence microarray readers or flow cytometric equipment. ◆

The identification of biological threats and the need to assess their impacts both globally and individually in the event of a bioterrorism attack have challenged us to take new measures to safeguard adequately against acts that could adversely impact national and economic security. Biomarkers can be used as indicators of normal biological processes, pathogenic processes, or pharmacological responses to bioterrorism agents such as bacteria, viruses, or toxins. Large fluorescent microarray readers, flow cytometric instruments, and mass spectrometric instruments have been used to quantify protein biomarkers. Analyses using such instruments are generally performed at centralized laboratories requiring extensive labor and analytical resources, plus they often involve lengthy turn-around times.

This project aims to develop novel nanoparticle labels and low-cost, portable electronic biochip devices based on biology, biosensor technology, microfabrication, and nanotechnology for the rapid and sensitive detection of protein biomarkers. A series of novel nanoparticle labels will be developed to enhance the sensitivity of immunoassay. Electronic biochips based on low-cost and disposable screen-printed electrodes will be used as immunosensing platforms for the rapid and specific detection of protein biomarkers. We expect that such quick, sensitive protein biomarker detection could provide an early warning of bioterrorist threats, hence minimizing the further spread of harmful biological agents and human casualties. Early detection of biomarkers is also essential for protecting and defending our water resources and food supplies against terrorist activity.



(A) Schematic diagram of the immunochromatographic electrochemical biosensor, (B) The photo of the prototype.

In FY 2007, we expanded nanoparticle labels for immunoassay of other protein biomarkers such as interleukin (IL)-1α. Nanoparticles were successfully conjugated with anti-IL-1α antibody. Transmission electron microscopy images indicate that nanoparticles do not aggregate after linking with the antibody. The nanoparticle-labeled antibody was used as the reporting antibody in an immunorecognition event. Electrochemical stripping analysis of the captured nanoparticles was used to quantify the concentration of IL-1α after an acid-dissolution step. The streptavidin-modified magnetic beads and magnetic separation platform were used to integrate a facile antibody immobilization with immunoreactions and the isolation of immunocomplexes from reaction solutions in the assay. The voltammetric response was highly linear, and the limit of detection was estimated at 0.3 ng mL^{-1} (18 pM).

In FY 2008, we developed a nanoparticle (NP) label/immunochromatographic electrochemical biosensor (IEB) for rapid, sensitive detection of protein biomarkers in human serum. This IEB integrates the immunochromatographic strip with an electrochemical detector for transducing quantitative signals. Made of CdSe@ZnS, the NP label serves as a signal-amplifier vehicle. A sandwich immunoreaction was performed on the immunochromatographic strip. The captured NP labels in the test zone were determined by highly sensitive stripping voltammetric measurement of dissolved metallic component (cadmium) with a disposable-screen-printed electrode, which is embedded underneath the test zone membrane. Several experimental parameters (e.g., immunoreaction time, the amount of antibody-NP conjugations and electrochemical detection conditions (e.g., preconcentration potential and time) were optimized using this biosensor for biomarker detection. The analytical performance of this biosensor was evaluated with serum samples spiked with a model biomarker. The results were validated with enzyme-linked immunosorbent assay and show high consistency. The results indicated that the IEB developed in this work is rapid, sensitive, and less expensive than other diagnosis tools. This IEB coupled with a portable electrochemical analyzer shows great promise for simple, sensitive, quantitative point-of-care testing of protein biomarkers.

Simultaneous Measurement of Fish and Flow Using Underwater Sonar

Zhiqun (Daniel) Deng, Marshall C. Richmond, Robert P. Mueller

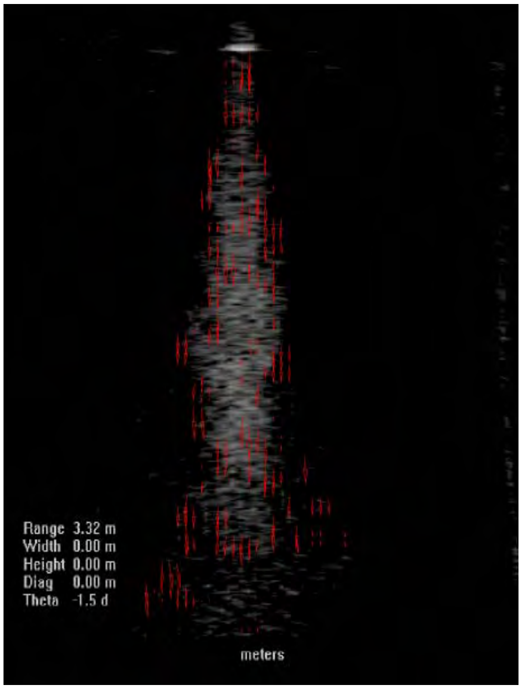
◆ This project demonstrates the feasibility of extracting water flow velocity using underwater dual-frequency identification sonar (DIDSON) images with cross-correlation techniques developed for laboratory particle image velocimetry (PIV) systems. Because DIDSON is in wide use for fish behavior studies, this technology can provide simultaneous, non-intrusive water velocity measurements in the immediate vicinity of fish, leading to a better understanding of the relationship between fish behavior and flow structures. ◆

Information required for the design of fish-friendly hydro-electric turbines is still lacking on the relationship between fish behavior and flow structures despite many years of research. Existing field characterization approaches conduct fish behavior studies and flow measurements separately and are coupled later using statistical analysis. These types of studies, however, lack a method for determining the hydraulic conditions or specific causes of the biological response. The DIDSON has been in wide use for fish behavior studies since 1999. The images within approximately 12 m of this device are clear enough to reveal fish undulating as they swim, distinguishing the head from the tail, and for users to measure fish during post processing. The maximum resolution at 3 m from the lens is 1.5 cm. The PIV is a state-of-the-art, non-intrusive, whole-flow-field technique that provides instantaneous velocity vector measurements in a whole plane using image cross-correlating techniques. There has been considerable research in the development of image processing techniques associated with PIV. This existing body of knowledge is applicable and can be used to process the images taken by the DIDSON.

The experiments were conducted in a water flume at PNNL's Aquatic Research Facility in March and June 2008. A laboratory jet flow was set up as the benchmark flow. When filled with water, the flume was 9 m long, 1.2 m wide, and 1.2 m deep. The nozzle began at a diameter of 25.4 cm, constricted to a 6.35-cm diameter over a length of 50.8 cm, and terminated through a tube 4.5 cm long and 6.35 cm in diameter. Different particles were used to seed the flow, which was characterized based on results from a previous project using laser doppler velocimetry (LDV). Exit nozzle velocities were set at 5 and 10 ft/s. A standard DIDSON operating at 7 fps and 1.8 MHz was positioned ~5 m from the jet nozzle and aimed at the underwater nozzle. Consecutive DIDSON images with known time delay were divided into small interrogation spots after background was subtracted. A cross-correlation was then performed to estimate the velocity vector for each interrogation spot.

After experimenting with existing measurements of the DIDSON software program, a window length of 1.25 m and a start range of 2.5 m were used to zoom in on the jet flow field. The lens focus was set to manual to improve the quality of acquired images. The DIDSON has a fixed resolution of 96 × 512 pixels, so the images need to be smoothed to increase the resolution to 400 × 512 pixels to provide enough horizontal resolution for cross-correlation. In addition, the DIDSON was operated at the maximum frame rate of 9 Hz to provide better temporal resolution and reduce the displacement of the particles within two frames. Tested seeding particles ranged from 1 to 5 mm in diameter and particles with 1 mm in diameter yielded the best results for images with a field of view of 1.25 × 1.37 m. Background images were acquired prior to the release of the seeding particles and subtracted from DIDSON images to improve the exposure of the particles. A typical velocity vector map is shown in the figure.

The average velocity in the core jet zone over the first nozzle diameter length was 1.61 m/s, which is comparable to 1.52 m/s measured by LDV. The spatial resolution of the vector map was not enough to compute shear or vorticity because of the small scale of this jet flow and resolution limitation of DIDSON images. However, this proof-of-principle project demonstrated the feasibility of extracting water flow velocity from underwater DIDSON images using image cross-correlation techniques.



Velocity vectors overlapped with DIDSON image.

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

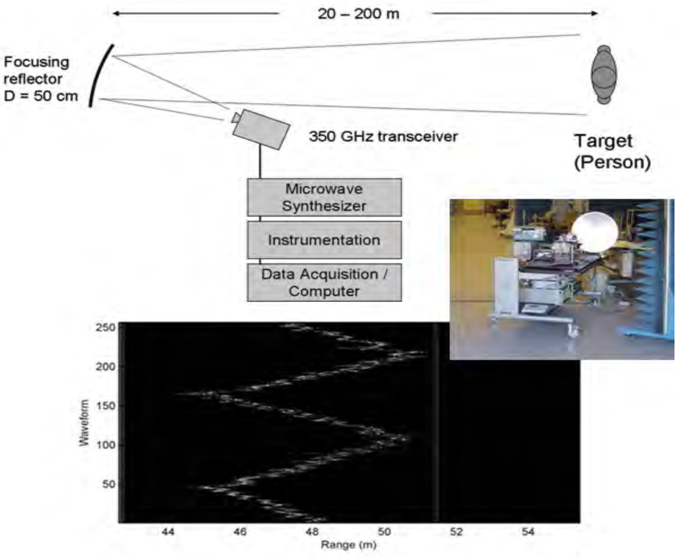
David M. Sheen

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

Millimeter (mm)-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 stand-off ranges (up to 100 m) do not yet exist. At these ranges, resolution achievable by mm- and sub-mm-wave systems is limited, which may not be sufficient to detect and identify concealed explosives. The objective of this project is to develop sub-mm-wave radar technology that detects concealed objects using non-imaging signatures that 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, extended range sensitive detection, clothing penetration, and variable nature of returns expected from the radar system. Sub-mm wave radar technology is promising for this application because it can penetrate clothing effectively, reflect from concealed objects, and propagate hundreds of meters without excessive loss.

A frequency range centered near 350 GHz has been chosen for this application by considering the trade-off between atmospheric transmission, excessive diffraction, and clothing penetration. A complete radar system has been assembled and is shown as a block diagram and photograph in the figure. A radar transceiver has been designed and fabricated at this frequency using a complex cascade of active and passive frequency multiplier modules driven by a microwave synthesizer and associated microwave electronics. This system transmits approximately 4 mW and is very sensitive due to the use of a heterodyne architecture. A spherically ground 50-cm diameter mirror is used to collimate the sub-mm wave beam. Initial measurements have been conducted using a small retro-reflector at ranges up to 50 m. The system shows excellent sensitivity using this target at these ranges, which indicates that the system will most likely operate up to 100 m with good sensitivity. The radar returns using human targets are expected to be significantly different than those obtained from the retro-reflector.



Experimental system configuration (top), photograph of experimental sub-mm radar system (right), and 350 GHz radar range time history data for a person walking slowly forward and back at a 50-m range (bottom).

A number of experimental time history measurements were collected from a human subject at 50 m without any concealed weapons. For each measurement, the subject was directed to move in one of several patterns, including standing relatively still, turning and walking slowly, and walking normally forward and backward. The data normally collected by the radar system are the in-phase waveforms over a frequency sweep of 344-356 GHz (12 GHz bandwidth) at a repetition rate of ~5 wave-forms/sec. A total of 256 waveforms were collected in each data set, which represents a time history of approximately 50 seconds. 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. An example result is shown in the figure, which is the radar returns for a man walking slowly back and forth in the beam of the radar system. The linear motion back and forth is readily apparent, as are smaller scale variations due to arm and leg motion with each step.

During FY 2009, this project will continue the cloth reflection measurements, conduct tests using mock suicide bombs/vest configurations, and perform cross-polarization experiments. Additionally, the radar system will be improved to provide higher bandwidth (up to 24 GHz), which will allow experiments with higher range resolution. Transceiver sweep and repetition time will also be greatly reduced, which will remove effects of subject motion during the waveform collection. Finally, data analysis and detection techniques will be developed.

Stand-off Infrared Detection of Explosives

Thomas A. Blake, Timothy L. Johnson, James F. Kelly, N. B. Gallagher

◆ The objective of this project is to develop a non-contact, eye-safe, optical technique for detecting and identifying explosive residues on the surfaces of vehicles and other objects, ideally at several meters stand-off. Technology developed from this work could be used in a portal monitoring scenario such as scanning vehicles as they move through a toll booth, check point, or port of entry. ◆

Stand-off detection of explosive residue left as first or second generation fingerprints can provide faster analysis of suspect containers and vehicles while working at a safe distance. Laser-based concepts are potentially feasible, but the best laser-induced breakdown spectroscopy requires high laser power that can readily damage eyes or surfaces to achieve requisite sensitivities. Passive or semi-active broadband infrared studies of surface radiance changes due to contact films may offer suitable sensitivity but require hyperspectral imaging information to help disentangle the complexities of real surfaces and their changes due to coatings. In order to work most effectively, infrared spectral radiometry techniques require advanced spatial and spectral filtering techniques both as part of the hardware and as post-processing algorithms to handle large data cubes efficiently and with requisite sensitivity.

The method being tested under this project uses infrared reflection-absorption spectroscopy for detecting contaminants on metal surfaces (painted and unpainted) at distances of 10 m or greater. Two instruments were used for this first year of the project: a PNNL-owned single-pixel Fourier transform infrared (FTIR) spectrometer and an imaging FTIR. These instruments were used outdoors, where the 1 sq m metal plates were placed at distances between 10 and 60 m from the two sensors. The plates were illuminated either by an active infrared light source (heat lamp) or by 220 K skyshine (illumination from the plates tipped back at a 45° angle). In addition to these field experiments, laboratory FTIR infrared reflection-absorption measurements were made of compounds, including HMX, $NaClO_3$, NH_4NO_3, Tetryl, RDX, TNT, and PETN, used to “contaminate” the plates in the field.

Using the imaging FTIR spectrometer and passive skyshine sensing technique, we were able to see chemical residues on the bare metal plates at distances between 10 and 60 m with areal dosages of between 15 and 90 micrograms of compound/cm^2. The chemicals were applied to the plates in an area ~30 cm in diameter. These preliminary target detection results are promising; however, we had difficulty seeing these same residues with the Telops imaging instrument when we were trying to detect the chemicals actively using the infrared light source shining on the plates. By contrast, we received excellent results with the single-pixel FTIR using a simple protocol to measure effective changes in reflectance, though we had difficulty seeing chemicals on painted metal surfaces with either set of concepts.

With the single-pixel FTIR instrument, we could easily see spectral signatures from explosives on bare metal surfaces using the active illumination. We were also able to see chemicals on steel and aluminum to 30 m with dosages of 40 micrograms/cm^2. Painted surfaces again presented some difficulties for detection of chemicals on those surfaces. We are continuing to test the detectivity of the single-pixel instrument for chemicals on various bare and painted metal surfaces using passive skyshine. However, since bare metals have no intrinsic molecular vibrations, they have no infrared active modes and are reflectors; infrared detection of trace contaminants on painted surfaces is thus inherently more challenging than on bare metals. We are optimistic that larger temperature differences will help improve spectral contrast.

During FY 2009, we will continue to examine the large quantity of imaging FTIR data collected and submit the results for a peer-reviewed publication. We will continue work with the single-pixel instrument, examining explosives coated onto various surfaces using different illumination and modulation techniques. On a somewhat different tangent, we noticed during the past year that some explosives will strongly discolor painted surfaces on a clear-coated commercial vehicle car door, so visible and/or SWIR detection of explosives on these types of surfaces appears possible. Finally, we will continue to pursue external funding for this work.

The outcomes of this project include: 1) development of key spectral radiance and reflectance change data for notable explosive compounds on metal and painted surfaces common to vehicles, shipping containers, 2) experiments will be conducted on a field-portable, focal plane array FTIR spectrometer to determine detection limits for both the surface contaminants and vapors, 3) data will be taken with a number of illumination configurations to assess best sensitivity for semi-active glancing-angle transits and nearer normal bistatic absorption-scatter situations, and 4) spectral images will be studied by both the infrared technology and sent to several independent groups to see if advanced hyperspectral imaging algorithms can be used to establish better statistical confidences for detection of residues.

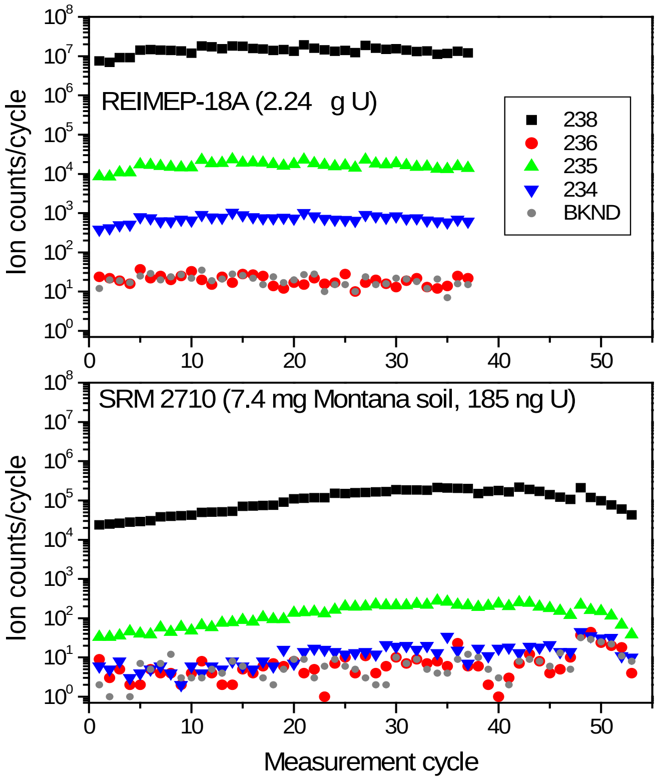
Ultratrace Uranium Isotopic Analysis without a Mass Spectrometer

Summer L. Ziegler, Bruce A. Bushaw

◆ The isotopic composition of uranium is important in a number of fields, including process control in the nuclear industry, environmental and health (bioassay) analyses, cosmo-nucleogenesis and chronology, and treaty inspection and/or verification. This project developed new laser-based methods for detecting and quantifying the minor uranium isotopes (^{234}U, ^{235}U, and ^{236}U) at ultratrace levels and lowered detection limits without using a mass spectrometer. ◆

A complete isotopic profile of the minor uranium isotopes can yield considerable information on the nature and history of a given environmental matrix. Levels of long-lived ^{234}U and ^{235}U are indicative of uranium enrichment compared with ^{238}U and the presence of ^{236}U (found in nature at 10^{-10} to 10^{-14} relative abundance) provides a unique signature for uranium contamination. Since the content of the minor isotopes can vary widely and independently, precise measurement of the full uranium isotopic profile is needed.

The isotope selective laser ionization spectrometry (ISLIS) approach is based on the uniqueness of atomic optical absorption lines that are distinctive for each element. At higher resolution, absorption lines are also distinctive for different isotopes, the so-called isotope shift. Small, single-mode diode lasers capable of resolving the isotope shifts are used to excite the targeted atomic isotopes sequentially in three steps to above their ionization limit (see figure). The use of three selective excitation steps provides an extremely high degree of elemental, isotopic, and isobaric selectivity, suggesting both the minimization of chemical separation requirements and the ability to distinguish between ions from isobars (e.g., ^{239}Pu and ^{238}UH$^+$; ^{236}U and ^{235}UH$^+$) and isotopes (e.g., ^{235}U, ^{238}U). Through this project, the excitation scheme for ISLIS uranium isotope fingerprinting has been optimized for excitation with small diode lasers and diode-tapered amplifiers.



Measurement of minor uranium isotopes from a uranyl nitrate standard (top) and a directly-loaded soil matrix (bottom) using the laser-based ISLIS method.

The high elemental and isotopic selectivity of the laser ionization process allows isotope-specific measurements without the need for mass spectrometric analysis, including precise 234:235:236:238 uranium isotope profiles and quantification of ^{236}U at sub-ppm isotopic abundances. The inherent selectivity of this technology should require minimal to no sample preparation prior to analysis, allowing the user to determine the uranium isotope fingerprint rapidly.

A series of analyses were performed to evaluate the degree of chemical treatment necessary prior to complex matrices analysis, including soil and shell matrices. We measured Columbia River sediment (NIST-SRM-4350b) as both a direct load and total digestate with promising results. Each sample had the equivalent of 1 mg of sediment (2.4 ng of total uranium). Continuing this work, we analyzed a contaminated soil matrix (Montana Soil, NIST-SRM-2710) that contains uranium at ~25 µg/g, an order of magnitude higher than the Columbia River sediment.

The figure shows uranium isotope ratios measurement using isotope selective laser ionization spectrometry. The upper graph is for a uranyl nitrate certified reference solution (REIMEP-18A) with near natural ^{235}U and ^{234}U abundances as well as a small amount of ^{236}U at relative abundance of ~3.1×10^{-8}. The lower graph is for a soil sample loaded directly into the graphite/titanium atomizer without chemical pretreatment or separation. Three of the four uranium isotopes were measured above background for the direct loaded soil matrix. This SRM soil measurement demonstrates that our selective laser ionization technology is capable of measuring the minor U isotopes directly without chemical pretreatment or separation in a small (under 10 mg) sample of complex matrix modestly contaminated with uranium.

We optimized the uranium signals by methods, such as ramping of oven heat, heat “bursting” the sample briefly to a very high temperature to anneal, or slow gradual heating to burn off excess matrix in the sample while maintaining the presence of uranium. We also evaluated and improved the graphite oven design using pyrometry for temperature profiling. We non-uniformly varied the bore diameter of both ends of the oven furnace to optimize the graphite tubes for uniform heating, which allows us to run operating conditions not at oven capacity extremes (i.e., lower voltage, same effective temperature for heating). The physical redesign of the graphite atomizer resulted in considerable improvement to the analytical, highly reproducible signal obtainable. The U-238 signal-to-background ratio improved to 4×10^6 with a μg-sized sample. The measured efficiency also increased to between 6×10^{-6} and 10^{-5} with a 40 ng aqueous standard. For both signal-to-background and overall efficiency, this is approximately a five-fold improvement over typical previous performance.

Overall project results include the optimization of the excitation scheme for diode lasers; a reduction in system size, weight, and power requirements; decreased routine sample size to nanogram levels; improved detection limits by an order of magnitude; improved precision to ~1%; analysis of complex matrices without chemical separation; and improved throughput via rapid measurements within one hour. The results from this project provide a solid proof-of-concept for the laser-based capability to measure uranium isotope ratios rapidly at trace/ultratrace levels with minimal to no pretreatment.

Understanding Ice Formation in the Atmosphere

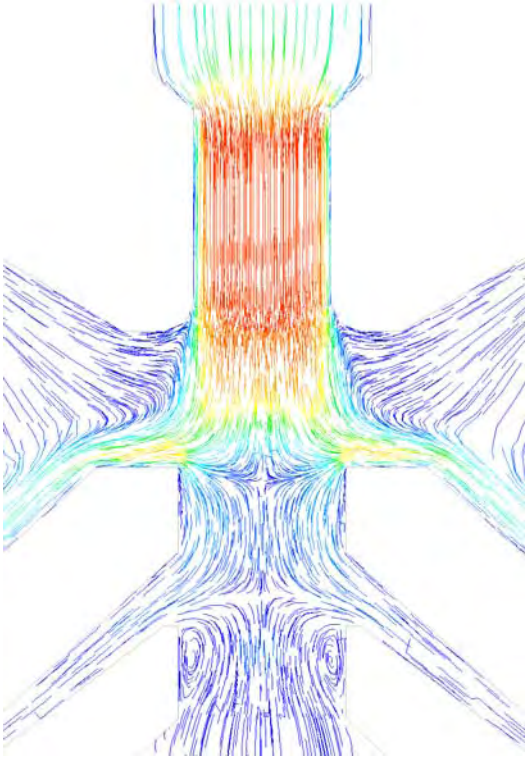
Daniel J. Cziczo, Gourihar R. Kulkarni, Mikhail S. Pekour

◆ 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 focus of this project. ◆

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

The formation of these liquid water clouds has been studied extensively. The indirect effect is typically subdivided into specific ways in which aerosols affect clouds, and the first and second indirect effects are purely due to warm clouds. This is not because they are the most important climatically, but instead because they are the most well-defined. Often at high altitude or far northern latitude, the remote location has made the study of ice clouds considerably more challenging despite the fact that ice crystals dominate the formation of precipitation and are understood to affect global climate due to the absorption and scattering of solar and terrestrial radiation. The ill-defined climatic impact due to ice crystals is normally known as the glaciation effect, a part of the indirect effect.

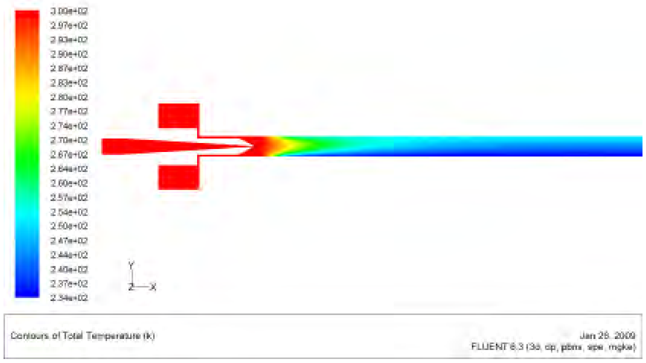
The objective of this project is to understand which aerosol particles initiate atmospheric ice formation. With an increase in our knowledge, we will be able to reduce the uncertainties of climate change and approach fully understanding the global water cycle. Specific foci include: 1) the determination of the exact conditions (such as the relative humidity and temperature) required for ice formation, 2) the effect that anthropogenic activities (for example, surface coatings of sulfate and organics) has on ice formation, and 3) how specific aerosol particles partition between ice crystals, cloud droplets, and unactivated, or "interstitial" aerosols. The objectives will be met by the development of two instruments. The first is a compact ice chamber that can mimic the formation of ice clouds. This is important because it decouples the need to go where ice clouds exist to study nucleation; instead, the ice formation mechanism can be studied at any location. Examples include urban centers to study anthropogenic activities or from light aircraft platforms, such as the Gulfstream 1, which can sample multiple locations in a short period of time. Second, a novel inlet system to separate ice crystals from unactivated aerosol and droplets will be developed, which will allow for the separation of crystals from ice clouds so that the material that initiated ice formation can be studied. Current inlet technology is beset with artifacts, and no inlet exists that can separate ice from aerosols and droplets from an aircraft platform.



Example of a CFD simulation performed in FLUENT to elucidate small-scale flow (eddies and vortexes) and transmission within a counterflow virtual impactor inlet showing velocity magnitude pathlines.

A design for the compact ice chamber was completed during 2008 in collaboration with the Swiss Federal Institute of Technology. The design phase encompassed two parts. First, an intensive computational fluid dynamics (CFD) modeling study was performed on the initial chamber design. This model indicated locations where high-precision machining was necessary (e.g., in the inlet area of the instrument where rapid changes in relative humidity and temperature occur). Another location of concern was joints in the chamber where eddies may develop, thereby creating uncertainty in the flow conditions and consequently lowering quality data. These CFD model runs were used iteratively to design, test, and redesign the chamber before any metal was actually cut. The hardware for the ice chamber is currently being fabricated at PNNL, with construction expected to be finished in early FY 2009. The CFD model also elucidated the cooling needs of the chamber, which allowed the refrigeration system for this unit to be designed in collaboration with Highland Refrigeration in Seattle, Washington. Further work on this will continue into FY 2009.

For the advanced inlet project, a conventional counterflow virtual impactor that can inertially separate cloud elements from aerosols has been constructed and is currently undergoing computation fluid modeling and testing. While counterflow inlets have been used for several decades, simple performance characteristics have never been resolved. These include the critical effect of misalignment on performance and possible breakup of ice crystals and water droplets due to aerodynamic stresses. The results of our model studies are being used to design advanced inlet technologies both by our group and others, such as our institutional collaborators at the University of California at San Diego. The importance of these results was highlighted by an invitation to present this work at DOE's Aerial Vehicles Program Instrumentation Workshop in October 2008. This study was also presented at the American Geophysical Union's fall meeting. A manuscript is currently being prepared for the peer-reviewed journal *Aerosol Science and Technology*.



Example of a CFD simulation performed in FLUENT of the temperature profile within the ice chamber. Notice the rapid temperature change near the inlet at the left side. This data have proven critical in the design of the cooling system.

As previously mentioned, the formation of ice crystals is the least understood area of the indirect effect. The formation of water droplet is better understood but does contain uncertainties in specific areas, one of which is also of interest within the scope of this project: the formation of water drops by mineral dust aerosol. Mineral dust is known to be a good ice nucleus, and future studies with the ice chamber will use this aerosol type. While it is known that the increase in land usage has also increased the atmospheric burden of mineral dust, it is unknown how this aerosol partitions between the ice, droplets, and interstitial phases. During FY 2008, we conducted a study of the drop formation potential of both idealized and real dessert dust samples for future comparison to ice nucleation studies. This study was deemed important enough to be invited as a paper at *Physical Chemistry Chemical Physics* for a special issue on the physical chemistry of aerosols, and a manuscript is in preparation.

During FY 2008, staff also continued to analyze preexisting data sets from Dr. Cziczo's work at ETH and Dr. Kulkarni's thesis data. As a result of these efforts, a total of four peer-reviewed journal articles on ice nucleation were produced, and four others are in preparation, not including those already mentioned. A total of three invited conference papers were presented, and five more are currently accepted for the aforementioned Instrumentation Workshop and the American Geophysical Union meeting.

In FY 2009, the compact ice chamber will be constructed and integrated with the cooling system with an anticipated completion of February 2009. Testing will ensue and will be performed in collaboration with University of Washington. We intend to field deploy this instrument at a mountaintop site in fall 2009. Based on the conventional counterflow virtual impactor that we are modeling and testing, the advanced inlet system will be designed and tested. This will be accomplished in the PNNL wind tunnel and/or from the G-1 aircraft platform. Final scheduling is pending but should take place in late fall/early winter 2009.

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, Richard C. Barry, Sam J. Harbo, Kevin R. Minard

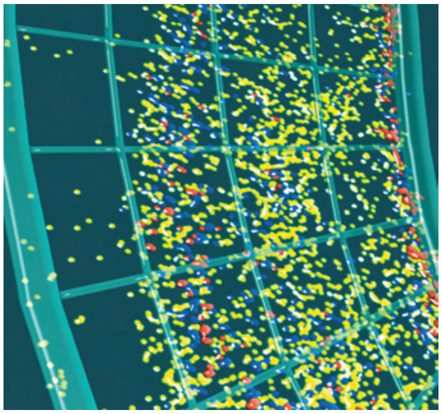
◆ Through joining biomedical data from different sources, this project aims to facilitate the prediction and understanding of biological pathways for environmental response and heart disease and to enable early detection, intervention, and amelioration of heart health challenges. ◆

Understanding mortality and morbidity associated with the heart is paramount to improving human health. An increasing amount of evidence is emerging that links natural and manmade environmental factors to cardiac diseases as well as often fatal decreases in heart muscle performance. In support of efforts to address this challenge, we will construct a multi-resolution framework of the mouse heart for organizing and analyzing different types of data modalities, including proteins, pathology, and magnetic resonance imaging. Our approach will establish a computational resource that will facilitate the development of a three-dimensional model for predicting and understanding the biological pathways of environmental response and heart disease. Further, the integration of these datasets offers an opportunity to link noninvasive magnetic resonance imaging (MRI) scans directly 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 the comparison of these with other data modalities. This challenge is compounded when one begins adding a spatial component to data that may be in two or three dimensions. Past efforts at identifying biomarkers and pathways in the heart have either used low-resolution whole-heart methods that lack spatial information or focused on specific quantities of information in isolation. Critically important to overcoming limitations of current experimental methods is the capability to organize accurately and reliably high-resolution data for the entire heart. Achieving this end will support DOE mission research and broadly benefit the U.S. research community.

We addressed this challenge by constructing a multi-resolution geometric framework of the heart suitable for storage and rapid online access to different data modalities. Using this 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. The framework will facilitate the discovery of biomarkers through the rapid integration of such datasets. We initially set out to build the foundation for achieving this goal by acquiring preliminary data from different sources and by constructing an initial set of two-dimensional computational geometry frameworks representative of the heart. 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 preliminary 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 the heart tissue slices were created using a subdivision-based deformable grid platform to represent the heart anatomy at multiple resolutions smoothly. Constructing a true three-dimensional heart framework will allow comparisons of normal with abnormal heart function and 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 discover biomarkers of disease phenotypes. For example, congestive heart failure is a condition without a cure that affects over 5 million Americans. Developing techniques for early detection and understanding the etiology of 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 would be powerful in delineating specific mechanisms. Further, the model would monitor and interpret environmental factors (e.g., particulates, chemicals, etc.) or drug therapeutics in real time relative to a standard heart atlas.



Spatial organization of biosignals in a geometric framework.

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

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

◆ We are using a "systems science" approach to gain an improved understanding of how carbon in the form of simple 5 and 6 carbon sugars is used for growth and fermented into ethanol by brewer's yeast, *Saccharomyces cerevisiae*. Our goal is to use that knowledge to engineer strains with increased efficiency for fermentation of xylose and arabinose into ethanol. ◆

The current rise in energy costs due to the increasing price of petroleum has moved biofuels into the U.S. collective consciousness. A large percentage of ethanol is made by the fermentation of glucose derived from corn starch using brewer's yeast, *S. cerevisiae*. However, for ethanol to become an economically viable alternative to petroleum-based fuels, several technical bottlenecks need 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 biomasses that have cell walls composed of cellulose and hemicellulose will need to be utilized as the carbon source to produce glucose and pentose sugars for ethanol fermentation. *S. cerevisiae* is unable to use the major pentose sugars that constitute hemicellulose, xylose, and arabinose. We plan to use genetics, metabolomics, and computational modeling to generate the data necessary for the 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 the 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. For example, metabolic and growth (i.e., biomass) information is used in the computational model to improve its predictive ability. Detection of metabolic bottlenecks can indicate the need for the higher (or lower) expression of a given gene product. Likewise, the computational modeling can point to unexpected bottlenecks that can be monitored through metabolic measurement and changed through genetic manipulation. We are also taking a forward (random or classical) and reverse (nonrandom or directed) 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 2008, we encountered an unexpected restriction site that was introduced into one of the promoters that was to be used for expression of genes from *Aspergillus niger* that metabolize xylose and arabinose (the deoxyribonucleic acid sequence dose is not identical to that published for *S. bayanus*). As a result, two strategies were taken to complete the cloning of the five genes that will be introduced into *S. cerevisiae*. The first strategy was to modify restriction site usage within the original cloning strategy; the second was to generate a new parallel cloning strategy in case of additional restriction site problems. All primers were ordered and received, and over 95% of polymerase chain reactions for the parallel strategies were completed. The final steps in vector construction are underway, and a purchase requisition was completed for deoxyribonucleic acid sequencing.

During the first months of FY 2009, the cloning vector deoxyribonucleic acid sequences will be examined for any errors introduced by the polymerase chain reaction. Once verified, yeast strains that contain the *A. nige*r genes for xylose and arabinose utilization will be used in genetic screens to select increased xylose and arabinose utilization. The goal is to alter the model to introduce genes that are responsible for xylose and arabinose catabolism into the yeast model and observe the effects on the metabolic model.

The final carbohydrate analysis method was defined and validated. In earlier analyses using samples from fungi that are known to utilize xylose and arabinose, there was a problem with the observation of the internal standard used in quantitation. This year, successful carbohydrate analysis was performed on both fungal biomass and spent media samples. 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. Next year's analysis will be performed both on the wild-type yeast and the one engineering to utilize arabinose and xylose.

At project completion, we expect to have identified pathways in *S. cerevisiae* that might inhibit the fermentation of xylose and arabinose to ethanol. We will also demonstrate that the knowledge gained through our multidisciplinary approach (genetics, genomics, and metabolomics) can be used to engineer a strain of *S. cerevisiae* that is significantly improved in the production of ethanol from xylose and arabinose.

Affinity Reagents Based on Novel Molecular Scaffolds

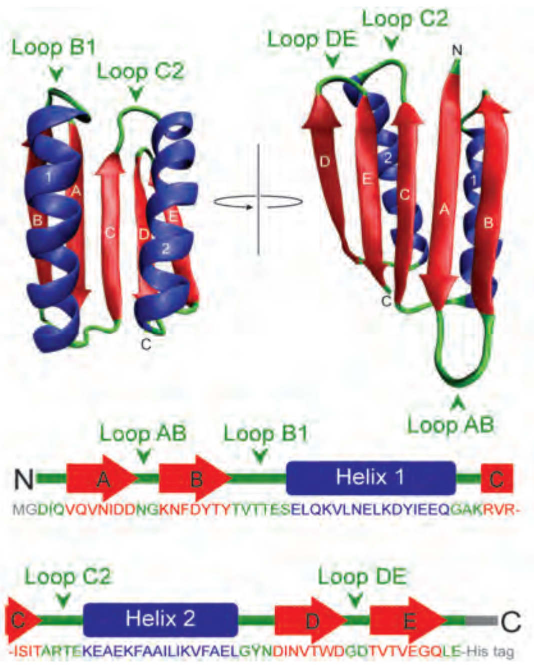
Cheryl L. Baird, Curt B. Boschek, Heather E. Engelmann

◆ The long-term goal of this research is to create a platform for high-throughput affinity reagent production based on a novel protein scaffold that is small, easily produced, and extremely stable. ◆

The demand for robust affinity reagents is rapidly growing for applications in proteomics and environmental and bio-threat detection sensors. Both applications rely heavily on affinity reagents that bind to a target and isolate it from a complex mixture. Biosensor applications have the additional requirement of the affinity reagent being functional in the field so that contaminants or threat agents can be detected at their source. In this case, the affinity reagent must be able to survive temperature fluctuations and complex samples encountered in the field. Currently, proteomics research and biosensor development have been limited and traditional methods for generating them cannot satisfy the demand for new, broadly applicable affinity reagents.

In FY 2008, our research was split between developing faster methods for generating phospho-specific immunoglobulin-based affinity reagents and investigating alternative proteins for use as affinity reagents.

Methods for Rapid Phsospho-Specific Antibody Generation. Most phospho-specific antibodies have a broad range of proteins containing phosphorylated tyrosines or serines (p-Tyr or p-Ser). To be useful for applications involving the study of phospho-regulated signaling pathways, antibodies are needed that recognize specific phosphorylation sites within a protein. The traditional hybridoma-based method for generating these antibodies takes about nine months and often produces reagents with poor affinity and specificity. To reduce production time, we started with an existing generic p-Tyr antibody and generated protein specificity through molecular evolution using random mutagenesis and selection with yeast surface display (YSD). We cultured three generic p-Tyr hybridoma cell lines purchased from ATCC (p-Tyr-1, FB2, 2G8.D6) and created three scFv antibody YSD libraries from the mRNA isolated from the cells. Analysis of these libraries showed low expression of full length scFv; unfortunately, none showed specific binding to a panel of peptides containing p-Tyr even when analyzed at high (100 µM) concentrations. Subsequent analysis of hybridoma cell lines IgG expression levels showed lower than expected yields (0.8-1 mg/L as opposed to 2-20 mg/L); however, the purified IgG did bind p-Tyr containing peptides (tested as conjugates to hen egg lysozyme). Potentially, antibodies in the scFv form displayed on yeast surface rendered them inactive or the hybridoma cloning IgG repertoire was ineffective.



The structure and sequence of Top7 with potential MRE insertion sites marked with arrowheads. The model is based on a 1QYS crystal structure.

Investigation of Affinity Reagents Based on a Synthetic Protein Scaffold. The immuno-globulin framework is the widely used scaffold from which affinity reagents are generated. However, this scaffold does not always produce reagents with the biochemical properties (affinity, specificity, durability) required for many proteomics validation and diagnostic applications. In FY 2008, we demonstrated that Top7, a synthetic protein with high thermal and chemical stability, could be engineered to bind a specific target and still retain its extreme biophysical stability. We rationally designed and characterized Top7 affinity reagents specific for the cell surface receptor by inserting a known MRE (CB1) for CD4 into four loop regions of Top7. The MRE is a 12-residue paratope-derived peptide from the CDR-h1 region of an anti-CD4 monoclonal antibody (clone 13B8.2).

In FY 2009, we will demonstrate that the Top7 scaffold can be used to generate a library of affinity reagents for broad application in biomarker validation and detection. Our past work on Top7 provides a foundation for the future development of rapid and efficient methods for generating Top7-based affinity reagents and demonstrating Top7's applicability to a much broader panel of targets, including intractable proteins that have failed to produce antibodies through traditional immunization methods. We plan to extend this work to investigate applications for Top7 affinity reagents that would benefit from its high stability. The eventual goal of studying Top7 as an affinity reagent scaffold is to have a method for developing an affinity reagent rapidly to any clinically or biologically useful target unlimited in application.

Analysis of Functional Diversity in Microbial Communities for Organic Carbon Transformations

Allan E. Konopka

◆ The increase in CO_2 fluxes to the atmosphere has raised global concerns regarding climate change. Carbon sequestration is one strategy being developed to mitigate CO_2 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. ◆

The understanding of microbial carbon sequestration in soil requires an ecological approach that takes into consideration the functional properties of microbial communities. Robust methods to analyze microbial functional diversity are a topic of current research. A variety of molecular-based tools have been used, including specific DNA probes and PCR primers as well as metagenomic analyses. We aim to develop two approaches: a novel method of stable isotope probing in which functional macromolecules (proteins) are labeled and physically separated, and the high-efficiency cultivation of microbes. The objective of this project is to develop new technical capabilities for microbial functional diversity analysis related to carbon biogeochemistry via analysis of functional proteins produced by soil microbes or via cultivation and analysis of the majority of soil microbes.

The technical achievements of this work will be protocols to label (with stable isotopes) and physically separate microbial proteins from soil microbial communities to further their subsequent proteomic analysis and implementing techniques to cultivate and screen rapidly the broad spectrum of microbes found in soil habitats at high relative abundance. Thus far, we have tested one strategy for high efficiency cultivation from soil.

During FY 2008, several elements related to microbial carbon cycling in terrestrial environments were investigated.

High Efficiency Cultivation Approaches. This work aimed to improve the efficiency of cultivating microbes from soil in order to produce biological material for a comprehensive analysis of genomic and physiological traits important for ecological success in terrestrial environments. Three strategies were tested, with all derived from the finding that in aquatic environments, cultivation efficiency was enhanced by inoculating microbes into a very low nutrient environment that replicated in situ conditions.

The first approach consisted of bacteria extracted from soil on filters that are incubated on the surface of moistened soil. The approach entails removing bacteria from soil particles and filtering them onto a polycarbonate matrix incubated on a moist soil surface. Previous work suggested that cells undergo limited divisions to form microcolonies. However, at PNNL, several technical problems arose with this method, particularly in terms of exogenous contamination, so other approaches were pursued, including the use of 96 well microtiter plates. This strategy involves a dilution-to-extinction approach that will lead to isolation of bacteria in the highest relative abundance. Because molecular analyses of soil systems indicate a high level of diversity with many bacteria at similar abundance levels, this could lead to the isolation of many unique microbes if carried out at high replication.

In the first strategy, the organic substrates used to cultivate microbes were groundwater or Columbia River water sterilized by filtration (remove all particulate organic matter) or autoclaving (retain natural particulate material). Relatively low concentrations (50 mg casamino acids per liter) were added to some formulations. The efficiency of cultivation was under 2%, which is within the range of results obtained with traditional microbiological techniques; thus, no improvement was noted with this approach. A third method was to use a liquid extract of soil organic matter as the carbon source based on a report in the literature that this stimulated soil bacteria growth. Liquid soil extract (SESOM) was prepared by suspending soils obtained from five disparate habitats into 10 mM 3-(N-morpholino) propane-sulfonic acid buffer at pH 7 and shaking at 200 rpm for 1 h. The extract was then filtered sequentially through Whatman paper and membrane filters with 5, 0.45, and 0.2 µm porosities to remove suspended particulate material and sterilize the matter.

Soil Inoculum	MPN/g Soil	St Dev MPN	Cells per g Soil	% Recovery
Pullman	1.62E+06	1.01E+06	9.31E+08	0.17
N393	2.93E+07	3.65E+07	2.70E+09	1.09
ALE	5.92E+06	6.86E+06	1.21E+09	0.49
Alabama	2.34E+06	1.48E+06	1.39E+09	0.17
Hanford	4.59E+04	NA	7.92E+07	0.06
Ringold	1.84E+05	2.78E+05	1.94E+08	0.09

Factorial experiments were conducted in which bacteria were removed from the various test soils and inoculated into each of the SESOM preparations, employing a dilution-to-extinction approach in microtiter plates. Samples were incubated for two weeks and analyzed by transfer to a solid bacteriological medium. The results were not significantly higher than found by traditional microbial approaches.

Stable Isotope Labeling of Soil Communities. We initiated work on the labeling of soil communities with isotopically labeled organic carbon or water with subsequent analysis of phylogenetically informative biomolecules. An experimental design in which soil was incubated with deuterated water and 12-C glucose or water and 13-C glucose was carried out. Phospholipids were isolated, and microbial community structure was determined by phospholipids fatty acid analysis. The community was dominated by proteobacteria (40% of total) and Firmicutes comprised ~20% and microeukaryotes 10% of total microbial biomass. These samples are waiting on analysis by isotope ratio mass spectrometry to determine biomarker fatty acid labeling, thereby indicating which microbial community members were significantly involved in carbon metabolism. This experimental approach represents a proof-of-principle that deuterated water can be applied as a general probe of microbial activity in natural systems such as terrestrial soils.

Biomaterials as Sequestering Agents for Radionuclides and Toxic Metals

Tatiana G. Levitskaia, Samuel A. Bryan, Thomas J. Weber, Karla D. Thrall

◆ Accidental or inadvertent intake of radionuclides is a national concern. Worldwide inventories and extensive use of radioactive materials in medical, industrial, and research activities enhances the risk of misuse by terrorists. Research from this project could significantly improve treatment procedures for individuals exposed to external ionizing radiation and/or radioactive materials. ◆

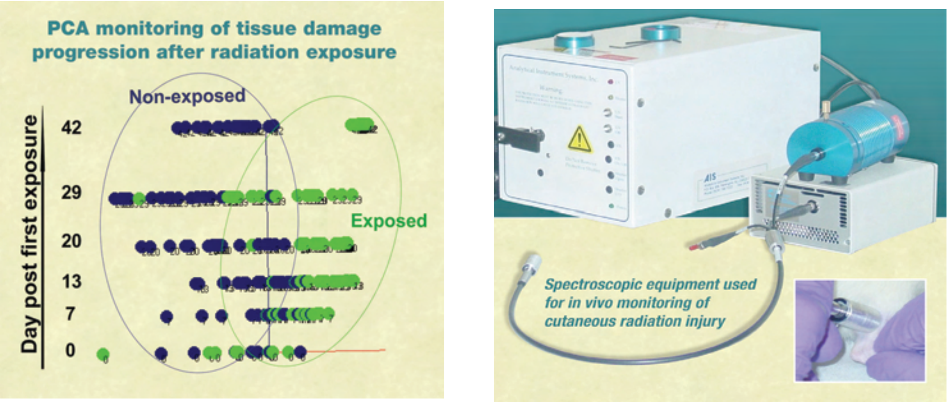
Radionuclides associated with terrorist activities exhibit different chemical and biological properties depending on their nature. Each radionuclide requires selective synthetic chelator. Natural receptors possess versatile chelation properties, and multiple functional groups make them capable of binding dissimilar metal ions. Our hypothesis is that natural chitosan materials are safe and orally effective decorporation agents for a wide range of radionuclides.

We studied the *in vitro* binding affinities of a commercially available chitosan oligosaccharide and its building block glucosamine for metal ions using potentiometric and spectroscopic techniques. Effective binding of the transition metal cobalt by chitosan oligosaccharide was observed. We found that chitosan preferentially binds cobalt in presence of a competing chelator lactate commonly found in living tissues. Our *in vivo* studies using laboratory rats showed that chitosan reduced the levels of deposited Nd(III) in living tissues by 20-43%, compared with those of untreated animals. These results suggest that chitosan is a promising agent for removing radionuclides from humans. By binding to radionuclides, chitosan would reduce their deposition in the critical organs and accelerate their removal to minimize internal radiation damage.

In addition to decorporation agents, medical countermeasures to radiation injury include radioprotectors, therapeutics for mitigation of molecular/cellular/tissue damage, and regeneration agents, including stimulating stem cells progenitors, immunomodulators, and cytokines/growth factors. It has been noted that naturally derived materials possess many of these properties and offer advantage of low toxicity, safe administration, and availability. In FY 2008, we tested chitosan and other biomaterials (including L-glutathione) for the prevention and treatment of radiation injury. Our results indicated that chitosan materials exhibit anti-inflammatory and hemostatic activities, promoting wound healing and attenuating the biological effects of ionizing radiation. Chitosan demonstrated similar beneficial activity in radiation/dermal wound combined injury treatment. Gamma radiation has been shown to deplete the cellular glutathione; we demonstrated that a combined administration of topical and systemic glutathione reduced the severity of cutaneous radiation injury and accelerated healing.

As part of this study, we evaluated the potential of using optical spectroscopy for non-invasive evaluation of the severity, progression, and effect of glutathione treatment on cutaneous radiation injury. Experiments demonstrated proof-of-concept that this technology can be used for conducting non-invasive, in vivo biodosimetry in partial body radiation exposures. An ultraviolet/visible spectrometer coupled fiber-optically with a reflectance/backscattering probe was tested to analyze the functional characteristics of radiation-exposed skin tissue from day 1 to 50 post-exposure in a Fisher F344 rat model. A principal component analysis of the data was successful in monitoring progression of the skin injury with time and differentiating between levels of exposure as well as between treated (topical and oral glutathione) and control animals.

Only limited techniques (high-frequency ultrasound) are available for the analysis of radiation skin injury. In the event of a nuclear/radiological emergency, methods are needed for assessing patients who potentially receive high radiation doses to the skin. Optical reflectance spectroscopy offers the advantage of rapid, non-invasive in vivo screening of potentially exposed population and follow-up monitoring of the progression of radiation skin injury and the effectiveness of treatment. Simple to use, this technology is based on the commercially available non-expensive instrumentation. It does not require special hospital settings or highly trained personal.



Monitoring of the radiation cutaneous injury by optical reflectance spectroscopy in F344 rat model (local 25 Gy gamma radiation exposure to the hind limb).

Biosignatures Discovery in Respiratory Exposure to Model Biological Agent Systems Using ^{1}H-NMR

Jian Zhi Hu, Nancy G. Isern, Bobbie-Jo M. Webb-Robertson, Kathleen McAteer, Donald N. Rommereim

◆ Early detection of inflammatory response and the ability to predict subsequent health outcomes after exposure to airborne biological agents will be accomplished through the discovery of metabolic biosignatures. ◆

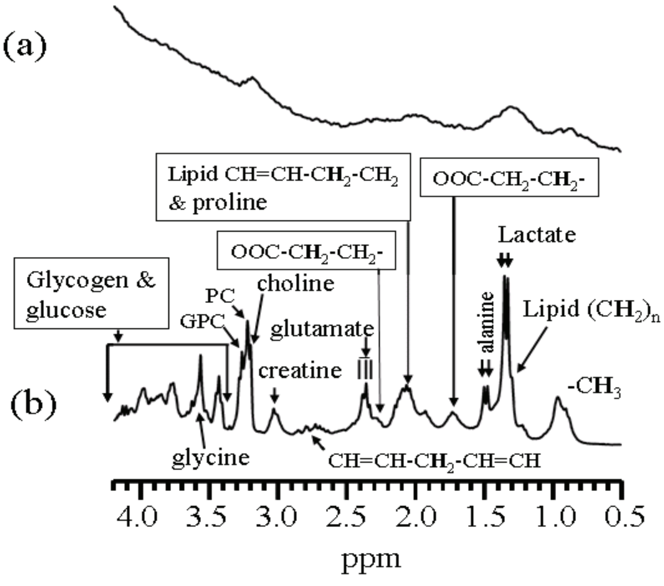
Interest in identifying potential metabolite biomarkers using non or minimally invasive techniques has increased. The goal of this work is the early detection of inflammatory response and the ability to predict subsequent health outcomes following exposure to various airborne biological abnormalities, including particulates and infectious agents.

Novicida of *Francisella tularensis*. Under this task, 60 lung samples from C57BL6 control mice and mice infected with Francisella tularensis (*F.t.n.*), genetically modified *F.t.n.* less virulent to mice, lipopolysaccharide (LPS), and pseudomonas aeruginosa (PA), respectively, from 4 to 48 hours post exposure were analyzed using our standard solution nuclear magnetic resonance (NMR) metabolomics. NMR free-induction decays (FIDs) were acquired on a Varian Unity 600 NMR spectrometer in a manual sampling mode. Datasets consisting of NMR FIDs were written to files and transferred to a workstation and processed. The Varian data FID files were converted to Felix format and multiplied by a squared sinebell decay function, then converted to frequency domain using fast Fourier transform. The spectral files were then imported to Chenomx NMR Suite 5.0 software for baseline correction, normalization, and binning using 0.01 ppm bins. This resulted in a final dataset that consisted of 324 bins. A large fraction of these bins had considerable variability and thus the data was further processed by a Kruskal-Wallis test across the various exposure classes. Multiple p-values were evaluated, and a bin inclusion p-value of 0.01 resulted in a final reduced dataset of the 36 samples with measured intensity values for 27 bins.

Statistical analysis of the ^{1}H NMR data in terms of classification accuracy (the number of correctly classified observations divided by the total number of samples) indicates ~61.1%, leading to a successful differentiation between the control, the mice exposed to *F.t.n.* (less virulent to mice), LPS, and PA with 62.1% of confidence.

Human Lung Inflammation and Scarring. Six anonymous human lung biopsy samples were shipped on dry ice from the University of Rochester for metabolic profiling. Three samples were clinically normal, while the other three lung biopsy samples were diagnosed as idiopathic pulmonary fibrosis (IPF). Each intact lung biopsy sample (i.e., without grinding or adding chemicals, including H_2O into the tissue) weighed ~65 mg and was loaded into our specially designed, completely sealed, slow-MAS sample rotor using a BSL-II cabinet. Immediately after loading, the outside of the rotor was soaked in a 6% bleach solution for ~3 minutes before moving to the NMR spectrometer. In this way, a BSL-II biological sample could be studied with a BSL-1 NMR spectrometer. The entire sample loading process took about 15 minutes in which little to no sample degradation occurs. Our unique slow-MAS ^{1}H NMR metabolic profiling were carried using ^{1}H PASS at a sample spinning rate of 80 Hz on a 300 MHz NMR spectrometer equipped with the slow-MAS capabilities.

We learned that slow-MAS ^{1}H PASS allows a high resolution metabolite to be obtained on intact human lung biopsy samples, and excellent quantification can be achieved using an external standard. All the metabolites found from our study of excised lungs from mouse can be found in human lung tissues. In addition, it is clear that concentrations of -CH_3, lipids, lactate, creatine, and 4-hydroxylproline are statistically significantly ($p < 0.05$) increased in lung tissues from patients diagnosed with IPF relative to normal lung tissues. These results are similar to those obtained from studies of excised lungs of C57BL/6 mice exposed to silica dust.



The water suppressed 300 MHz ^{1}H NMR spectra of a human lung biopsy: (a) the static spectrum obtained by traditional NMR, and (b) slow-MAS ^{1}H PASS spectrum obtained at 80 Hz.

Community-Based Biosignatures of Exposure and Functional Response in the Sediment-Water Interface of the Hyporheic Zone and Periphyton Community in River Systems

Amoret L. Bunn, David R. Geist, Craig A. McKinstry, Ann L. Miracle

◆ Microbial communities of freshwater and subsurface ecosystems are being evaluated to identify biosignatures of community identity and function that correlate to movement of contaminants in those ecosystems. In particular, biosignatures from uranium exposure are being evaluated in the periphyton community of the sediment/water interface and the hyporheic zone where groundwater and river water mix. ◆

Biosignatures that indicate change in the biotic community due to the presence of contamination in the sediment-water interface can be used as part of monitoring programs assessing remediation activities. Groundwater mixes with river water beneath the streambed in an area known as the hyporheic zone, within which microbial communities and periphytic communities (biofilm primarily composed of algae and diatoms) on the surface of the river bottom will be exposed to and potentially impacted by contaminants. This project screened the phylo-genetically diverse periphyton community for biosignatures in response to uranium exposure. Our research efforts will contribute to developing integrated ecosystem predictive models for application at sites addressing uranium contamination through the sediment-water interface of aquatic systems.

Exposure studies were used to benchmark standard ecotoxicological methods for risk assessment with biochemical and molecular methods of biosignature discovery in an effort to validate those latter techniques as viable and appropriate for monitoring contaminant impacts in the field. Concurrently, we designed, constructed, and are operating a hyporheic mesocosm for use in conducting controlled, laboratory-based studies on physical and biological aspects of hyporheic zones as they relate to contaminants surface waters from groundwater sources. As with the uranium-exposed periphyton, samples from the hyporheic mesocosm were evaluated for biosignatures using new methods being developed.

Results from the uranium periphyton bioaccumulation study showed that the bioaccumulation of uranium by periphyton were at similar rates as found in FY 2006 for the 10 and 100 µg/L uranium exposures, and the rate for the new 500 µg/L uranium exposure was also within the range of other tested concentrations. There were no signs of toxicity at any of the uranium concentrations, which is contrary to other studies that show toxic responses in phyto-plankton as low as 5 µg/L. One biosignature screen (phospholipid fatty acid analysis) was not sensitive to uranium exposure and time.

Several design changes were implemented to the hyporheic mesocosm in FY 2007. Smaller systems were used to evaluate biofouling on the inlet screen, and results indicated the importance of covering weir chambers for control. A new groundwater/sediment chamber was designed to control the flow regime within the sediment. River water flow was regulated with graduated cobbles at the inlet of the sediment in order to control turbulent flow and erosion within the groundwater/sediment chamber. Sediment sampling systems were being tested for use in destructive coring of mesocosm at the end of summer. Samples from the hyporheic system were evaluated using the new biosignatures screening tools.

The hyporheic mesocosm was then sampled in January 2008. The mesocosm was used to conduct preliminary screening of a microbial community's response to silver nanoparticles using ribosomal intergenic spacer analysis. This work was re-scoped for FY 2009 to investigate the fate, transport, and transformation of nanoparticles in aquatic systems. Nanomaterials that are being used in commercial products (e.g., sunscreens and antimicrobial textiles enter the environment directly or indirectly through waste water treatment plants). Since the materials that are made into nanoparticles are durable and recalcitrant, the accumulation of these materials in the environment could be significant over time and lead to unforeseen impacts on the ecosystem.

Under this new effort, we are choosing to examine silver nanoparticles. The increasing use of products with nanosilver correlates with the growing possibility of release of Ag into the environment through a number of different waste streams. Based on the results of our efforts in FY 2008, the complexation of silver with other chemicals and organics is a crucial factor in its bioavailability and toxicity; and therefore, the aquatic environment receiving effluents containing nanosilver must be considered before applying laboratory-derived data concerning uptake and toxicity.

Results from this project, and specifically, the hyporheic mesocosm is the subject of a presentation at SETAC North America. The phospholipid fatty acid analysis of the FY 2007 uranium periphyton bioaccumulation study using non-linear statistical learning was the subject of a paper submitted to *Proceedings of the National Academy of Sciences*.

Development of a Computational Model for the Eelgrass (*Zostera marina* L.) and its Demonstration in Puget Sound for Studying the Effects of Climate and Human Driven Stressors on Eelgrass Distribution and Food Web Function

Ronald M. Thom, Irvin R. Schultz, Gary A. Gill, Sharon E. Hook, Tarang P. Khangaonkar,
Lyle F. Hibler

◆ This research will develop a unique modeling tool to demonstrate effective sub-lethal indicators of single and multiple stressors on an important marine ecosystem. This tool would be a fundamental breakthrough in the integrated decision-making process for managing ecosystem health and benefiting the resource-based economy in coastal ecosystems. In addition, this tool would inform ongoing modeling efforts, as well as help us integrate more effectively the measures of ecosystem function with ecosystem health. ◆

Coastal ecosystems worldwide are suffering the effects of multiple stressors associated with activities carried out on land and in the nearshore zone. At the same time these systems are changing to absorb the impacts of large and small-scale natural factors. By grasping the interaction and impacts of multiple anthropogenic factors on a coastal system, and measuring them against a backdrop of large scale natural factors, management systems can better adapt to current and future conditions, and ameliorate the most extreme effects of ecosystem change on human systems and benefits.

The goal of this project is to develop a predictive capability to assess the response of eelgrass ecosystems to the stresses of climate change and human disturbances and contamination. Our research will develop a computional modeling approach that allows interactions between individual models of aquatic organisms to create a virtual ecosystem, which would permit models of important habitat-forming species (such as eelgrass) to interact with models of both microbial communities and animal populations (such as important invertebrate and vertebrate species). The eelgrass ecosystem forms a tractible ecosystem for testing the general response of aquatic habitats to climate change as well as human-derived stressors, including contaminants associated with oil, wastewater, and stormwater discharges. Through an intregrated approach of model simulation and focused experimentation, we will use the ecosystem model to demonstrate our capability to parse out fundamental mechanisms that produce responses as well as practical key biomarkers, which indicate eelgrass ecosystem health.

We anticipate that this project will lead to development of a predictive capability to assess the response of eelgrass ecosystems to the stresses of climate change as well as human disturbances and contamination. Specifically, we will:

- Develop a conceptual model that will form the basis for a numerical computational model that predicts eelgrass ecosystem conditions and links to existing models of fish populations dependent on eelgrass during critical life stages
- Develop the numerical computational model based on the conceptual model and experimental results from mesocosm experiments
- Link the eelgrass ecosystem model to the Puget Sound hydrodynamic circulation model and through model simulations test the impact of climate change on water quality variables such as temperature on the eelgrass population and associated animal species.

The following project milestones were achieved during FY 2008:

- Reviewed the literature for seagrass models to understand the breath of current models developed
- Conducted a formal review and preliminary testing with a model at the U.S. Environmental Protection Agency's (EPA's) laboratory in Newport, Oregon
- Modified and corrected the EPA model to meet our objectives and determined additional aspects of the model we would want to incorporate
- Conducted workshops (that ultimately led to a draft collaborative research plan) with National Oceanic and Atmospheric Administration (NOAA) staff, Washington State Department of Natural Resources (WDNR) Eelgrass Stressor team, and the EPA to understand the practical issues that could be addressed with an integrated eelgrass model
- Published a paper on light required to support eelgrass growth and survival, which is a critical factor in the eelgrass model.

A proximal goal in FY 2009 is to link the ecosystem model with output from the hydrodynamic circulation model of Puget Sound presently being developed by others at PNNL. The Puget Sound model can be used to predict both climate change effects on water properties as well as the transport of contaminants in tidal systems. The combination of mechanistic-response based biological and ecosystem models is a powerful capability to offer regional and national ecosystem managers.

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 is developing new chemical cross-linking and informatics methodologies to speed up the identification of protein complexes that are the cellular machinery of all biological systems. The developed technologies will yield comprehensive information about the machinery of cells and microbes, enabling the rational reengineering of cellular pathways (for example) 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 holds great promise for helping to solve energy-related challenges and addressing needs related to global climate change. Under current growth and environmental conditions, microbes efficiently perform many functions relevant to DOE mission needs, such as hydrogen production. These natural processes are not tuned or perfectly engineered for technological uses. A major obstacle when attempting to tune or reengineer biological systems is lack of knowledge of the key interoperating biomolecules; technology that can provide a snapshot of the biological machinery under appropriate conditions is required. Chemical cross-linking of proteins has the potential to be that enabling technology.

Cross-linking has been used for validating known partners in a protein complex and identifying interaction sites but not for the global discovery of novel protein complexes and interactions. To achieve that goal and therefore discover how 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. To this purpose, we have assembled a multidisciplinary team with strengths in analytical chemistry, bio-organic chemistry, bioinformatics, and biology.

Ubiquitin sequence, crystal structure (pdb:1V80), and color coded cross-linking sites identified by developed cross-linking technologies. (^) represents sites of identified lysine cross-links.

In this project, we are developing novel methodologies related to global cross-linking. The long-term goals of the research are to cross-link simultaneously all protein complexes from the living cell and use mass spectrometry-based techniques to identify the complex members 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, we are building upon advances in mass spectrometry capabilities to develop a transformative technology to identify cellular protein machines. Since this project's inception, we have successfully assembled pieces for discovering and characterizing protein complexes in intact live cells. Specifically, we have 1) synthesized a novel protein cross-linking reagent, 2) synthesized a related reagent for enrichment and optimized enrichment of cross-linked species, 3) performed mass spectrometric characterization on enriched cross-linked species, and 4) performed preliminary cross-linking experiments of complex membrane fractions.

Using ubiquitin and other model systems, selectivity of the cross-linker toward primary amine functionality was confirmed. We were able to identify several specifically cross-linked species validated by inspecting the protein structure and finding that distances are reasonable between the amine-containing amino acids for which cross-links were found. Methods for enrichment were developed and successfully applied with this protein, permitting identification of additional species. We also observed the expected reporter mass signal in mass spectra of the cross-linked species. In addition, we were able to pioneer the coupling of two different forms of mass spectrometry for cross-linked samples, further increasing identification confidence.

We have thus synthesized, characterized, and validated our prototype cross-linking reagent and capture validation reagent as well as the whole methodology. Based on this initial success, we are now ready to test the enrichment strategy on a complex sample and work out the relevant informatics algorithms to identify cross-linked species. This ability will yield information about working molecular machines in living microbes not currently available but needed to harness optimally these microbes to produce biofuels and sequester carbon dioxide.

Early, Validated Biomarkers of Infectious Diseases in Humans

Timothy M. Straub, Rachel A. Bartholomew, Cynthia J. Bruckner-Lea

◆ Growing cells outside the host (*in vitro*) in a manner that allows the cells to differentiate into tissue structures that behave physiologically similar to the hosts from which they were derived (*in vivo*) allows us to study mechanisms of infectious diseases in ways not previously possible. In this project, we developed *in vitro* tissue models to study human infectious diseases. Our work may allow development of methods for rapid triage that can prevent casualties in the event of a bioweapons attack. ◆

There is growing concern that data regarding mechanisms of infectious diseases in humans, whether generated from traditional *in vitro* tissue culture or *in vivo* animal exposure studies, do not extrapolate well with the course of disease in humans. Dr. Cheryl Nickerson, currently at the Biodesign Institute Center for Infectious Diseases and Vaccinology at Arizona State University, provided expert training to the project team in generating physiologically relevant cell culture models for infection with viral and bacterial pathogens. The method we used grows cells on porous collagen-coated beads in rotating wall vessel bioreactor systems under conditions of physiological fluid shear. This allows the cells to differentiate into multiple cell types for the respective tissue from which they were derived and in their native three-dimensional architecture. Our project objective was to use these three-dimensional cell cultures to develop infectivity assays for both human viral and bacterial pathogens and identify unique but orthogonal host biomarkers of infectious diseases. The ultimate purpose of this project was to develop sensor platforms for rapid triage following a bioweapons attack. To identify these biomarkers, PNNL researchers worked to identify metabolic volatile organic compounds and secreted peptides indicative of host innate immune response, respectively.

In the second year of this project, we published our results on the first *in vitro* cell culture infectivity assay for human noroviruses using the three-dimensional human small intestinal model (*Emerg. Infect. Dis.* 13(3) 396-403). The products from our norovirus infected cell cultures were provided to related, but different LDRD projects, whose work showed that identification of biomarkers from these infected cell cultures was possible. In addition, the physiological relevance of the three-dimensional cell cultures was demonstrated by failure to infect a three-dimensional model of large intestinal epithelial cells with human noroviruses. This was a significant finding because human volunteer studies in the 1970s only showed infection of the small (not the large) intestine. Failure of infection was further confirmed by the inability to find biomarkers of infection that can be differentiated from non-infected cells.

Further work with *Salmonella typhimurium* of a three-dimensional large intestinal model confirmed the findings of our collaborator, Dr. Nickerson. Metabolic volatile organic compounds and peptides were different from the biomarkers identified for human norovirus infection. A *Pseudomonas aeruginosa* infection of three-dimensional lung epithelial cells showed that we could reproduce the fermenting "grape-like" first reported for pure cultures of the bacteria. Both of these studies are significant in that infection with different pathogens produces different biomarkers. This is important when developing sensor platforms because it implies that unique biomarkers can be identified (and then detected on a sensor array), and it allows for rapid triage and identification of infectious diseases that enable immediate action to treatment and circumvention of mass casualties.

During FY 2008, our research was focused on the *F.t.n.* infection of a three-dimensional lung epithelial model. This subspecies is infectious in rodents but generally not in humans. Our work confirmed this finding, and we are now ready to compare and contrast results with the pathogenic subspecies *tularensis* and *holarctica*.

FopA Assay

Harvest Time (hrs post infection)	***Ftn* Minus A549 (control)**		***Ftn* Infected A549**	
	Mean Ct Value	**Standard Deviation**	**Mean Ct Value**	**Standard Deviation**
24	35.37	0.18	33.96	0.84
48	35.50	0.29	34.40	0.46
72	37.07	0.11	35.33	0.42

Summary of mean Ct (Taq Man real-time PCR cycle threshold whereby a positive detection is instrument determined) values for each set of *Francisella tularensis novicida* (*F.t.n.*) control and infected A549 cells. The mean Ct represents a minimum of triplicate infections for each time point: 24, 48, and 72 hours post infection.

Ecophysiological Investigation of Cyanobacteria Using Controlled Cultivation

Johannes C.M. Scholten, Thomas O. Metz, Eric A. Hill

◆ A mission within DOE's Office of Biological and Environmental Research is the microbial production of biomass-derived hydrogen to move the world from an oil-based to a hydrogen economy. Our research on the development of a two-stage photobiological biohydrogen production process from water and sunlight using *Cyanothece* sp. *51142* is an excellent model system that will enable movement toward such an economy. ◆

The evolution of oxygenic photosynthesis in cyanobacteria approximately 2.5 billion years ago transformed the Earth's atmosphere and allowed for the evolution of all oxygen-consuming species. Cyanobacteria still hold a pivotal role in the ecology of the planet. In the oceans, a major contributor of carbon fixation on the planet, more than half of the photosynthetic organisms are cyanobacteria. This project seeks to develop a systems-level understanding of these organisms to appreciate and exploit fully their potential contribution to carbon sequestration, alternative energy production, and environmental restoration.

Photobiological hydrogen production ("biophotolysis") from water and sunlight is one of the most popular and appealing renewable energy sources being considered today. Both direct and indirect biophotolysis processes (without and with intermediate CO_2 fixation, respectively) have been proposed and investigated. However, current conceptual and experimental approaches to photobiological hydrogen (H_2) production face a number of near-insurmountable scientific and economic problems, including the back-reaction of O_2 with H_2, safety issues in direct biophotolysis, and the high cost of photobioreactors in both direct and indirect processes. In addition, yields approaching 10 moles H_2 per mole of glucose are needed to meet DOE year 2015 cost objectives. At present, yields greater than 4 H_2 per glucose have not been achieved.

We propose an alternative process that physically separates O_2 from H_2 production, avoids the need for expensive photobioreactors in the H_2 generation stage, and should increase yields by generating more intracellular energy. This process is based on a plausible mechanism using known metabolic pathways, and it could be relatively low cost while achieving realistic efficiency goals for overall solar-to-hydrogen conversions. The proposed two-stage process uses cyanobacterial mass cultures for high solar efficiency intracellular carbohydrate production in low-cost open ponds coupled with a dark oxygen-limited fermentation to produce high yields of H_2.

Efforts in FYs 2005 and 2006 resulted into a design of novel photobioreactors with a high aspect ratio (tall and skinny) to optimize light penetration during growth of photosynthetic organisms. The photo-bioreactors developed at our laboratory were installed at Washington University in St. Louis and Purdue University, where staff were trained by PNNL staff in operating the reactors. Further, we provided technical assistance to the university researchers to help them keep the reactors running properly. As a result, we proposed that all controlled growth experiments with cyanobacteria have to be done with a constant source of carbon dioxide, the control of which would allow better interpretation of other diurnal cycle experiments.

In FY 2007, *Cyanothece 51142* was grown in a bioreactor under continuous cultivation in the light (LL) and dark (DD). A number of rates were tested to determine the maximum growth of the organism under LL and DD conditions. Our results suggested that the *Cyanothece 51142* cells became limited for CO_2 during our dark cultivations but not for light. During the cultivation, cell samples were taken for metabolomics analysis, as well as optical density, dry weight, CO_2 consumption, and O_2 production. The LL samples were compared with samples obtained during different growth rates (LL vs. LL) and pooled LD samples obtained from the diurnal rhythms experiment. In both cases, there were observable differences in the LC-MS chromatograms, suggesting that growth rate (LL vs. LL) and cultivation conditions (LL vs. LD) may result in different metabolite profiles or even a whole metabolome. Additional metabolomic measurements are being done to confirm our initial results.

In FY 2008, we grew cells for microscopic, proteomic, and metabolomics analyses to identify and characterize dynamic changes in morphology, protein expression, and metabolite production that are important to comprehending mechanisms involved with the circadian rhythm of *Cyanothece*. The high quality cells grown in our bioreactors were used to discover something significant about circadian rhythms in cyanobacteria. We determined that cell division occurs once per day a few hours into the light phase of 12-hour light/dark cycles and that a small death phase occurs a couple hours before the end of the light phase. Using custom automated cell-density sensors and manual measurements, we determined that our automated cell-density sensor more accurately predicted cell numbers than manual spectro-photometric measurements. Online monitoring of population changes during controlled cultivation allows us to improve growth of Cyanobacteria and algae for biomass or biofuels production. The growth data provided by our bioreactors is being used to construct a model of Cyanothece growth.

Field-Deployable Nanoparticle Biosensor

Irvin R. Schultz, Marvin G. Warner

◆ This project will demonstrate that immobilized antibodies attached to magnetic nanoparticles injected into a bivalve can provide a 100- to 1000-fold increase in sensitivity for the detection of chemical and biological warfare agents (CWA and BWA, respectively). Ultimately, this project will allow bivalves to be a simple yet highly effective naturally occurring sensor for warfare agents. ◆

Prior research established that filter-feeding bivalves can capture CWA breakdown products and BWA surrogate bacteria from the water. This is an important finding because bivalves such as mussels are good model organisms for monitoring fresh- and saltwater environments in close proximity to activities of concern in coastal, Great Lake, and inland waterways. However, a serious limitation of using bivalves for monitoring CWA and BWA is that agent levels must be very high relative to detection capabilities requiring that sampling occur during peak exposure periods at or near the site of agent release. Our experimental approach seeks to overcome this problem by using immobilized antibodies attached to a nanoparticle and injected into the Mediterranean mussel (*Mytilus galloprovincialis*), a common bivalve.

The use of protein-conjugated nanoparticles provides a number of significant advantages for a variety of deployment scenarios. First, the nanoparticles offer a scaffold on which we can immobilize not only full-length antibodies and proteins but also peptide and fragments often used as affinity reagents for CWA and BWA detection. In both cases, the nanoparticle scaffolds can serve as a stabilizing platform that will impart increased stability to the protein reagents, extending their operational lifetimes. Second, since nanoparticles can be synthesized to nearly any size from 1-2 to over 100 nm, it is possible to tune the structure intimately to provide a persistent material in the mussel for an extended time, an obvious advantage in that these materials could be deployed and sampled with no loss due to specimen rejection or excretion. To that same end, the size and functionality of the nanoaparticles impart true solubility to the materials rather than dispersiblity, leading to settling commonly observed in larger polymer particles (diameters above 100-200 nm). Finally, the use of secondary antibody labeled semiconductor quantum dots as the optical signaling modality allows us to exploit desirable properties (i.e., extreme brightness, photostability, multiple emission colors from a single excitation source) to enable trace detection of materials concentrated in the mussel over the sampling period.

Research focused on establishing the preferred nanoparticle for conjugation studies and initial evaluation of the nanoparticle biosensor using as a model toxin, domoic acid. The studies were performed as part of two specific aims described below.

Optimal Nanoparticle Size for Maximal Retention in Bivalve Hemolymph. We tested three different nanoparticles varying in diameter from 5.8 to 50 nm that were suspended in a synthetic molluscan saline solution and directly injected into individual mussels. Hemolymph was then removed periodically from the mussels and the nanoparticles extracted magnetically and gently rinsed. The washed, concentrated nanoparticles were then solubilized in hot concentrated nitric acid, and the total iron content was determined by inductively coupled plasma-optical emission spectroscopy (Perkin-Elmer model 4300) using matrix matching and standard calibration curves. Results indicated that the 5.8 and 25 nm particles exhibited similar retention characteristics in the bivalves and appeared to undergo minimal clearance from hemolymph. Thus, the 25 nm particles were selected for continued study due to lower cost and better availability from commercial sources.

Nanoparticle-Antibody Conjugation to Determine Pharmacokinetics and Functionality of Antibodies After Injection. We tested two different antibodies (a monoclonal and polyclonal) that bind to domoic acid. We determined the optimal procedure for coupling antibodies to the functionalized nanoparticles using glutaraldehyde as a cross-linking agent. After covalently attaching the antibodies, the particles were mixed at 4°C over night, and a sample of the supernatant before and after mixing was taken to determine protein concentration. These measurements indicated that antibody loading rates on the particles ranged from 30-70 µg antibody per mg nanoparticles. After coupling, the particles were mixed in Tris buffered saline for 30 minutes to block unreacted sites. The coupled antibody-nanoparticle sample was then re-suspended in PBS (pH 7.4) and stored at 4°C until use with mussels.

Saline suspensions of each antibody-nanoparticle conjugate and unconjugated nanoparticles (used as a control) were injected into separate groups of mussels. After 20 and 50 days post-injection, mussels were transferred to a microcosm containing various concentrations of the domoic acid toxin (0.01, 0.1, and 1 µg/ml). After 24 hours, hemolymph samples were removed from each mussel, the domoic acid concentration measured, and a separate aliquot of hemolymph used to assess binding affinity toward domoic acid. Results indicated that mussels injected with nano-particles conjugated to the monoclonal antibody had approximately twice the hemolymph concentration of domoic acid compared with the control mussels. In addition, approximately 7-10% of the domoic acid in the hemolymph was captured by the conjugated nanoparticles. These promising findings demonstrate that the domoic acid antibody retained functionality after injection into the mussels.

The results from FY 2007 established the proof-of-principle that nanoparticle antibody conjugates retain functionality toward the antigen for an extended time (over 3 weeks) within mussels. However, the two-fold improvement in detection of the antigen (domoic acid, in this case) is unlikely to be adequate for successful use as a biosensor. Thus, research in FY 2008 focused on two phases for improving the methodology for loading mussels with nanoparticles. Phase 1 was directed on improving retention of the Fe_3O_4 nanoparticles within the mussel and Phase 2 on alternative dosing procedures that would increase the concentration of circulating Fe_3O_4 nanoparticles within the mussel.

Results from Phase 1 activities indicated that a critical aspect of the nanoparticle physical property was the ability to remain in a dispersed state in hemolymph and seawater. This became apparent in studies using Fe_3O_4 nanoparticles coated with either glutathione or polyacrylic acid. These surface coatings were initially selected because they allow nanoparticles to form stable suspensions in physiological saline solutions. However, after addition to hemolymph or seawater, nanoparticles were observed to aggregate and settle out of solution. Additional studies revealed that Fe_3O_4 nanoparticles coated with polyethylene glycol (PEG) were able to form stable suspensions in seawater and hemolymph, which improved mussel retention after intravascular injection.

Subsequent experiments performed during Phase 2 explored the feasibility of loading mussels with the PEG-coated nanoparticles by water exposure. Individual mussels were placed in 1 L Pyrex beakers filled with 0.5 L of Sequim Bay seawater. The solution was spiked with nanoparticles, and both uptake from the water and concentration of the nanoparticles in the mussels was measured as before, relying on total Fe analysis. The results indicated that the PEG-coated nanoparticles were rapidly absorbed by the mussels, with essentially all the nanoparticles spiked into the beaker eventually absorbed by the mussels. Initial results from ongoing experiments indicate that the nanoparticles are better retained by the mussels compared with findings from intravascular injection. Collectively, these results indicate a strong potential to improve biosensor sensitivity by using Fe_3O_4 nanoparticles coated with PEG and relying on water uptake as opposed to intravascular injection to load the mussels with the nanoparticle-antibody conjugate.

Fine-Scale Physical Structure and Microbial Composition of Soil Aggregates Related to Carbon Sequestration

Vanessa L. Bailey, Scott E. Baker, Brian Lower

◆ The aims of this research are to integrate cutting-edge imaging and genomic strategies in developing a three-dimensional representation of a soil aggregate and its intrinsic microbial community. This analysis will be used to determine the variation in community structure between aggregates. ◆

The storage of carbon in soil is potentially able to offset substantial greenhouse gas emissions, yet the degree to which the carbon-carrying capacity of a soil is biologically driven or physically controlled is unknown. Thus, we conducted physical analyses of individual soil aggregates in tandem with genomic analyses that will describe the composition of the microbial community in each aggregate.

Three decades ago, pioneering soil microbiologist David Jenkinson described the soil microbial biomass as "the eye of the needle through which all organic materials must pass [into the soil]." Generally speaking, soil microbial biomass rarely exceeds 2-3% of the total soil carbon. One must investigate the soil microbial biomass in greater detail to understand how it contributes to the stabilization of soil carbon and thus how it may be manipulated to enhance soil carbon sequestration on a scale that could conceivably reverse rising levels of greenhouse gases in the atmosphere. The soil microbial biomass transforms nearly all organic material that enters the soil, retaining some carbon for growth, some as extracellular metabolites, and respiring some as CO_2. Some of the retained carbon persists in recalcitrant forms and is stabilized in soil; however, part of the stabilization is also attributed to physical protection mechanisms. The controls on and balance between these two mechanisms of carbon sequestration is unknown.

We began this research with a collection of individually stored and labeled soil aggregates all less than 1 mm in diameter. Parallel research led by Ken Kemner of Argonne National Laboratory collaboratively analyzed the study aggregates prior to our analyses. He made transmission X-ray microtomography measurements on the soil aggregates, generating high-resolutions "CAT" scans of each aggregate. After the samples were returned, we extracted DNA from each individual aggregate, which was then pyrosequenced using primers designed to interrogate a highly variable region of the bacterial 16S rDNA, yielding a census of the organisms inhabiting each aggregate. At a high level, we hope to identify which groups of bacteria are consistently present in aggregates sharing certain physical features (e.g., pore size distribution, aggregate size). We have had regular communication with Dr. Kemner and with Dr. Lee Ann McCue, who led a project analyzing the pyrosequencing data in order to integrate the two data sets.

Contact- and tapping-mode as well as phase-contrast atomic force microscopy (AFM) will be employed to image the aggregate surface. Briefly, an AFM probe consisting of a sharp tip (radius on the order of 10 nm) is raster-scanned across a sample surface using a piezoelectric scanner. Changes in the tip-sample interactions are monitored using a laser beam reflected off the AFM probe and onto a position-sensitive photodiode detector, thereby generating a three-dimensional topographic image. In phase-contrast imaging, the phase angle of the AFM probe is monitored. Changes in phase angle during scanning are related to energy dissipation during tip-sample interaction (e.g., attractive or repulsive forces) and are due to changes in the sample surface chemical composition. A phase-contrast image will allow us to examine the nanometer-spatial distribution of organic (biological) versus inorganic (mineral) material on heterogeneous samples. Since tapping-mode and phase-contract imaging can be conducted concurrently on the same sample, we will be able to acquire simultaneous topographic and phase images that can be compared with the same aggregate or between aggregate samples.

We demonstrated that useful DNA could be extracted from extremely small quantities of soil, a significant challenge in this project. The pyrosequencing data was returned and initially indicates that there are a set of approximately nine bacterial groups that are consistently represented in the individual aggregates, far smaller than the number of groups reported even in pooled samples of these aggregates. The results of this six-month project have been used as the foundation for a subsequent proposal to a PNNL initiative, and we hope they will provide support to future external funding proposals.

Much of what is known about the structure and biology of soil aggregates has been learned separately. Classical soil science approaches for examining both have been constrained by the mass of sample needed, necessitating pooling of aggregate size fractions where approaches used are often destructive, where different aggregate pools have been required for multiple analytical streams. Current PNNL cutting-edge technology and expertise have the ability to transcend these constraints and could be integrated to yield one of the first targeted dissections of a soil structural component for both physical structure and biological composition.

Functional Genomic Analysis of the Regulation of Bone Cells by a Bioactive Lipid

Norman J. Karin, Sue A. Karagiosis

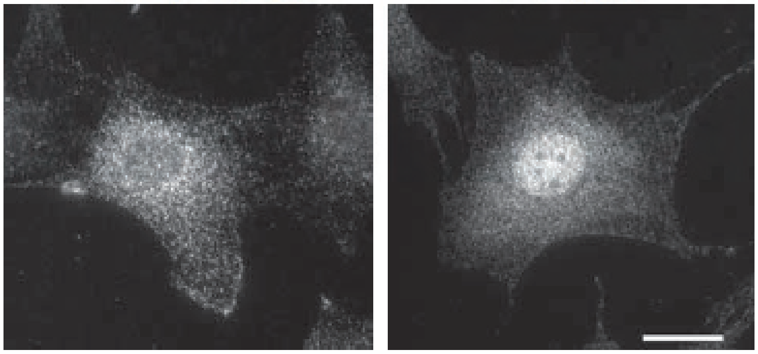
◆ Lysophosphatidic acid (LPA) is a lipid growth factor known to stimulate soft tissue healing. This research is focused on the ability of this factor to regulate bone cell function and provide valuable new insights into the control of skeletal health and the cellular mechanisms of bone healing. This project may lead to new additives to surgical implants used in the treatment of traumatic bone loss, such as in injuries sustained by soldiers wounded by explosive devices. ◆

Our overall goals were to identify factors that promote bone formation and to elucidate the intracellular signaling mechanisms that govern bone cell function. LPA is a water-soluble lipid generated by platelets during blood clot formation and soft tissue wound healing. Recent data have led us to postulate that lysophos-pholipid stimulates bone regeneration. Data generated in previous project years revealed that bone-forming cells (osteoblasts) are highly sensitive to LPA, and this lipid stimulates a variety of osteoblast functions *in vitro*. This project was designed to determine the effects of LPA on bone cell function and the intracellular pathways responsible for these effects.

Osteoblasts *in vivo* often become entrapped in the skeletal matrix where they differentiate into osteocytes and survive for decades. These cells are characterized by a highly dendritic morphology coupled with the ability to form a junctionally connected mechanosensory network in bone matrix. The function of this intercellular network is thought to be the basis for beneficial effects on the skeleton of weight-bearing exercise, as well as the loss of bone mass in the absence of physical stimulation, such as during extended exposure to microgravity associated with long-term spaceflight. We developed an assay to measure osteocyte membrane outgrowth and made the novel discovery that LPA is a potent inducer of dendrite formation. Data from this phase of the project resulted in non-LDRD work to determine mechanisms by which osteocytes respond to physical stimuli such as gravitational force, a process that we hypothesize requires LPA production by bone cells.

We performed a mass spectrometry-based proteomic analysis of osteocytes to identify a broad spectrum of responses to LPA, which led to the identification of more than 13,000 peptides from osteocytes cultured in the presence/absence of LPA. Filtering of low abundance proteins resulted in a dataset of more than 7000 peptides. Using statistical methods developed at PNNL, we identified 284 and 844 proteins that exhibited significant changes in abundance after cells were treated with LPA for 6 and 24 hours, respectively. Most proteins identified as LPA regulated were not previously known to be expressed by osteocytes. Gene ontology annotations revealed that a number of the LPA-regulated proteins are linked to phenomena that might have major roles in the control of membrane extension, such as cytoskeletal elements and adaptors, adhesion molecules, and proteins involved in the motility and establishment of cell polarity. These data will be presented at the annual meeting of the Orthopaedic Research Society in 2009.

We also continued our efforts to identify signaling pathways activated in LPA-treated osteoblasts. We observed the activation and concomitant nuclear translocation of ERK1/2, an enzyme that is an essential nodal component of many key signaling pathways. The results of our efforts in FY 2008 revealed that ERK1/2 activation is a key regulator during the LPA-induced osteoblast motility process, an essential cellular function component of bone fracture healing. Further, our data showed that activation of ERK1/2 in LPA-treated osteoblasts is independent of the epidermal growth factor receptor transactivation and intracellular Ca^{2+} signaling, two pathways that are linked to ERK1/2 activation in most other cell types. This finding points to a novel mechanism by which osteoblasts stimulate ERK1/2 in response to the lipid factor. These data led to a national scientific meeting presentation and a submitted manuscript to a major journal.



Nuclear translocation of ERK in LPA-treated mouse osteoblastic cells. The cells were genetically engineered to express a fluorescently labeled form of ERK1. Control cells exhibit ERK1 fluorescence primarily in the cytoplasm. After five minutes of exposure to LPA, a significant fraction of fluorescent ERK1 appears in the cell nucleus. This phenomenon is linked to the ability of activated ERK to regulate gene expression in LPA-treated osteoblasts. The scale bar represents 15 μm.

Identification of Proteomic Profiles and Biosignatures in Complex Microbial Systems Absent of Genomic Sequence Data

Scott E. Baker, Ellen A. Panisko, Matthew E. Monroe, Kevin K. Anderson, Don S. Daly

◆ Microbes occupy a variety of ecosystems, and changes in their protein expression profiles may serve as sensors from environmental stressors. This project will develop a widely applicable capability to perform proteomic fingerprint analyses in an ecosystem or microbial community where the genomes of constituent organisms have not been or cannot be sequenced, thus overcoming the gene annotation requirements of many proteomics methods. ◆

Uncovering biological changes in an ecosystem using a global proteomics strategy offers great promise. Current global proteomic strategies, however, are dependent on the existence of a genome annotation database for each organism under study that limits the utility of uncovering changes in ecosystem proteins by high-throughput identifications, and therefore potential biomarker discovery to systems with organisms whose genomes have been sequenced. In this study, we propose to circumvent this critical limitation by conducting a relative comparison of putative peptide profiles regardless of their initial identifications. The ecosystem-level putative peptide profiles would be obtained using current proteomic identification algorithms that use a comprehensive non-redundant protein database to match experimental and virtual/database generated spectra. A suite of internal standards will be used for sample-to-sample and run-to-run normalization. Thus, genome-specific annotations that are unattainable for almost all ecosystems would not be needed to compare changes in the ecosystem protein profile across conditions. Crucial to this effort is the ability to determine the amount of any given peptide across a number of samples or experimental conditions. Our experiments will initially use a single model organism, *Trichoderma reesei*, before moving to more complex microbial communities resident in river ecosystems (i.e., periphyton).

Under this project, we describe liquid chromatography/mass spectrometry (LC-MS) peptide abundance estimates with a linear model featuring all-important terms to account for unequal peptide LC-MS measurability. We advance fitting this model to an often incomplete LC-MS data set with REstricted Maximum Likelihood (REML) estimation, producing estimates of model goodness-of-fit, treatment effects, standard errors, confidence intervals, and protein-relative concentrations. We illustrate the model with an experiment featuring a known dilution series of a complex *T. reesei* protein mixture.

For the 781 of 1546 *T. reesei* proteins with sufficient data coverage, the REML-fitted mixed-effects models capably described the LC-MS measurements, whose terms effectively accounted for this significant source of uncertainty. Ninety percent of the relative concentration estimates were within 1/2 fold of their expected relative concentrations. Akin to the common ratio method, this model also produced slightly biased estimates. Bias decreased significantly, both absolutely and relative to the ratio method, as the number of observed peptides per protein increased.

A number of quantitative methods exist for LC-MS-based proteomics. The majority of these make use of stable isotopes either by cellular, mid- or post-processing peptide labeling (ICAT, ITRAQ, and 18O), or isotopic peptide spiking (AQUA). These methods are limited by the number of both relevant isotopes available and comparable samples or peptides from any given experiment. In addition, metabolic labeling of samples requires the use of a defined minimal media. The technique developed in this study does not require the use of stable isotopes, peptide labeling, or isotopically labeled peptides; rather, it relies on the direct measurement of a peptide's intensity, a traditional database search to group peptides by protein, a robust set of technical and biological replicates, and a statistical model to account for processing error (in particular, differences in LC-MS measurability across peptides) in the observed intensity. The advantage of this method over labeling added during sample processing is that it reduces the amount of sample handling involved, thereby minimizing the amount of sample loss and contamination. Because there is no limit to the number of conditions or treatment combinations, complex experiments that involve a number of experimental samples (e.g., a multipoint time-course experiment) are straightforward to design, execute, and analyze using established statistical methods. This technique also avoids another limitation of metabolic labeling, which is the requirement to use defined minimal media.

During FY 2008, we developed, validated, and published in a peer reviewed journal a putative peptide profiling experimental technique with *T. reesei* samples and developed and validated a putative peptide profiling technique using existing data, where existing data were used from *T. reesei* samples spiked with internal standards (statistical analysis). Furthermore, we applied the proteomic/peptide profiles method to periphyton exposed to uranium.

Interrogation of Glucose Metabolism by Oral Biofilms Using Combined Nuclear Magnetic Resonance/Optical Spectroscopy and Stable Isotope Labeling

Paul D. Majors, Jeffrey S. Mclean

◆ Bacteria in nature often form mixed cultures containing multiple interacting species and biofilms, which are aggregates of cells attached to surfaces and to one another in an extra-cellular polymeric matrix. Biofilms are found in nearly every natural environment, and they beneficially or detrimentally affect energy, environmental health, and industrial processes. Currently, there are no adequate experimental methods to study bacterial biofilm metabolism in order to link this information to species function. This project has developed methods to gain an improved understanding of biofilm function that will vastly improve our ability to manage these important processes. ◆

Although most bacteria are members of mixed-community biofilms, our current understanding of microbial metabolism is based almost entirely upon single-species planktonic cell studies. These single-species studies do not necessarily correlate with their behavior when present in complex multi-species biofilms, nor do they account for the role played by other uncharacterized species present in these communities. This knowledge gap is a result of the prior inability to study metabolism directly in live biofilms. Dental plaque is one of the best-described mixed-species bacterial communities, yet it is barely understood despite years of research. Thus, microbial metabolism is not only a relevant health-related system, but it is also a convenient organization for demonstrating the functional analysis of biofilms in general.

Most of what is currently known about bacterial function has been extrapolated from studies using non-aggregating pure cultures. Under this project, we developed the requisite tools for the functional analysis of intact mixed-species biofilms. Specifically, we combined nuclear magnetic resonance (NMR) methods with stable isotope probing (SIP). NMR provides information on the collective biofilm metabolic function, while SIP of nucleic acids [DNA and RNA]-incorporated carbon-13 from labeled substrates identifies the key microbes that catalyze these metabolic processes. Viable, functioning model oral biofilms containing up to 10 species have been defined; thus, they constitute a logical system for developing new biofilm characterization technologies, as analogous environmental model communities are not yet available. The successful application of these combined approaches to address oral biofilm function have the potential to address questions regarding metabolism affiliated with other complex microbial communities.

During the first project year, our work focused on 1) developing the infrastructure needed to conduct live, ex situ oral biofilm studies, 2) adapting the experimental NMR configuration to provide a model environment relevant for oral biofilm studies, 3) developing a capability for SIP analysis, and 4) performing physiological studies of *Streptococcus mutans* biofilms. Progress included reproducible cultivation of *S. mutans* biofilms, development of a chemically defined medium for ex situ biofilm NMR/SIP studies, and the performance of initial *S. mutans* glucose-metabolism studies under varying chemical conditions. We found that the metabolite profiles and concentrations were impacted by the presence of oxygen. Other progress included initial testing a new experimental configuration that was expected to provide improved metabolite detection under conditions that conform more closely to natural oral environments and use natural enamel biofilm-support surfaces.

In FY 2007, *S. mutans* biofilm metabolism was studied under normal and cariogenic (low pH) growth conditions by NMR and high-pressure liquid chromatography methods. Depth-resolved transport measurements were developed and correlated with biofilm structure and metabolism. In parallel study, SIP technology was used to study glucose metabolism in natural (mixed species) juvenile human dental plaques. These studies revealed the metabolically active species and their collective biofilm function under healthy buffered (pH 7) conditions.

During FY 2008 (the final project year), both NMR and SIP were used to study juvenile human dental plaque samples under buffered and reduced pH conditions to simulate caries disease progression (pH = 4.5-5.5). Plaque samples were presented with C13-labeled substrate (glucose or lactic acid, a primary glucose byproduct). Samples were monitored in real time by NMR spectroscopy, showing the formation of organic acids (lactic, acetic, formic, and pyruvic) responsible for tooth decay. As opposed to parallel samples used in the previous year, the NMR samples were subsequently analyzed by SIP, which identified the active species at low pH (disease) conditions and those species capable of utilizing lactic acid under disease conditions. The final results are being analyzed and will be published later this year.

Isoform-Specific Quantitative Proteomics Applying N-terminal Enrichment and Informatics Deconvolution

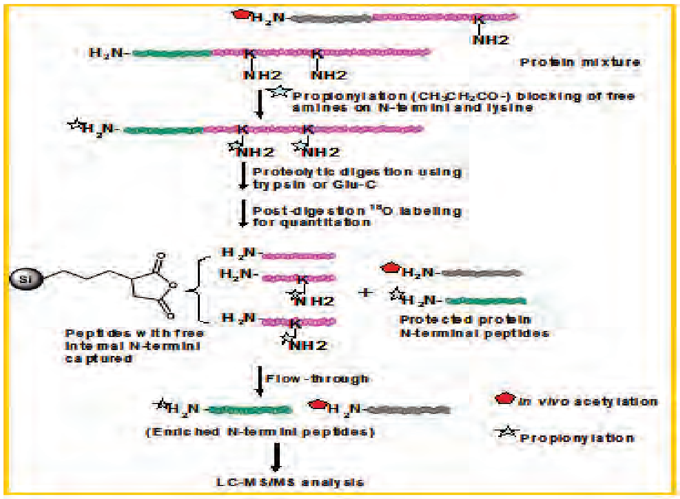
Wei-Jun Qian, Xu Zhang, Ashoka D. Polpitiya

◆ The ability to create different protein isoforms by alternative splicing and proteolytic processing is a major mechanism for cellular function control; additionally, various protein isoforms have been linked to human diseases. The quantitative measurement of specific protein products or isoforms that participate in a functional network may be essential for deciphering cell signaling and could represent the next era of proteomics. This project focused on the development of a novel protein N-termini enrichment strategy for quantitative analysis of isoform-specific protein abundance changes by specifically targeting N-terminal peptides. ◆

In higher eukaryotic organisms, a single gene typically produces multiple protein isoforms with similar sequences via alternative splicing, post-translational modifications, and proteolytic processing. The ability to create different isoforms is a major mechanism for cellular function control; in addition, various protein isoforms have been linked to human diseases. Proteolytic processing plays an essential role in many physiological processes and pathologies by regulating protein functions through the specific hydrolysis of peptide bonds within proteins. Thus, it is essential to measure quantitatively the specific isoforms and proteolytic protein fragments that participate in a functional network for both systems biology research and biomarker discovery efforts. Generally, the current “bottoms-up” proteomics strategy is ineffective for the characterization of protein isoforms; therefore, there is a critical need to develop a proteomics approach that will enable global quantitative analyses of protein isoforms in complex proteome samples.

This project focused on developing an innovative approach for enriching protein N-terminal peptides and having necessary informatics tools for data analysis so that each protein isoform can be specifically identified and effectively quantified based on its positional information from the N-terminal peptide. The figure shows the scheme of our N-terminal peptide enrichment strategy that consists of two novel steps: 1) an initial blocking step on all N-termini and lysine residues at the protein level by propionylation with propionic anhydride, and 2) the isolation of tagged N-terminal peptides after enzymatic digestion in a single step that involves removing all other (internal or C-terminal) free-amine containing peptides using amine-reactive silica-bond succinic anhydride beads commercially available from Silicyle. The propionylation step introduces a unique 56 Da tag on all N-termini and lysines so that the *in vivo* acetylated N-termini (a 42 Da modification) will be distinguished from the chemically tagged N-termini. Following these reactions, the derived protein samples will be digested using either trypsin or endoproteinase Glu-C. The peptide samples can be further labeled with ^{18}O for quantitative analyses by post-digestion ^{18}O exchange. The peptide mixture will then be incubated with silica-bond succinic anhydride beads, which captures all free amine-containing internal peptides, allowing specific enrichment of tagged N-terminal peptides for LC-MS/MS analysis.

We initially demonstrated the effectiveness of this N-terminal peptide enrichment approach by achieving above 95% efficiency for propionylation and identifying 211 different N-terminal peptides from a mouse plasma sample. We believe that the successful development of this approach will be valuable for biological research such as cancer biology by generating specific new information related to proteolytic processing as well as specific protein isoforms. This N-terminal proteomic approach is also of significance for identifying post-translationally modified N-termini. Moreover, the effective enrichment of protein N-terminal peptides will lead to reduced sample complexity, thus allowing potentially more low-abundance proteins to be identified.



Schematic diagram of the N-terminal peptide enrichment strategy.

Iterative Modeling of Host-Pathogen Interactions

Jason E. McDermott, Liang Shi

◆ This research supports DOE's mission to achieve major scientific discoveries and provide scientific facilities by developing approaches to tackle the modeling of multicellular systems. Developing tools to build useful, detailed, multi-scale systems models of these systems will help achieve DOE's missions in bioenergy, bioremediation, and carbon sequestration. ◆

Building useful computational models of biological systems is difficult and largely uncharted. The great amount of high-throughput data available for many systems and the advent of novel high-throughput experimental techniques provide an opportunity to develop detailed molecular models, but they 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 the construction of large-scale models that could address significant biological questions.

The host-pathogen interaction represents an attractive target for computational models for several reasons. The interaction between the bacteria *Salmonella enterica serovar typhimurium* (STM) and its primary target of replication in the host 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. The establishment of an approach for multi-scale modeling in multi-organism systems will have impact in many areas of systems biology.

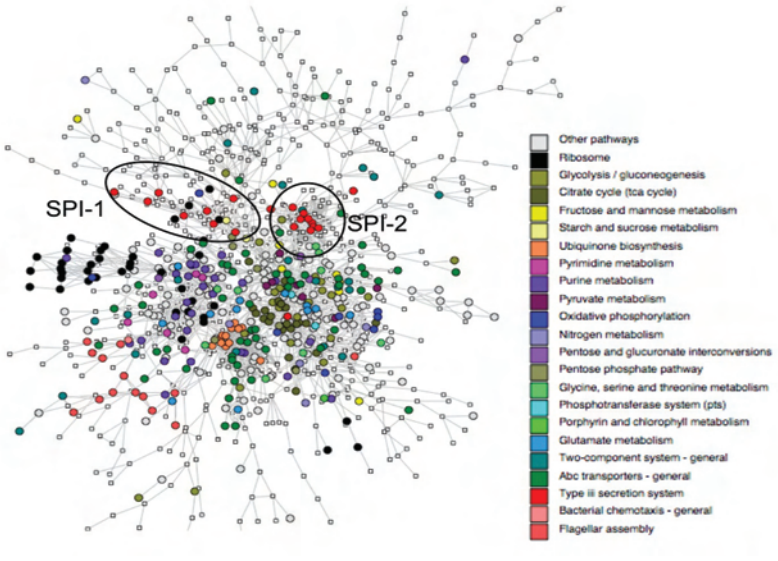
In FY 2008, we developed computational and experimental approaches to modeling the functional and regulatory networks of STM relevant to virulence. Additionally, we began to build models for the host mouse macrophage as it responds to infection by STM and stimulation of the innate immune response.

Functional and Regulatory Networks in STM and Host Response in Mouse Macrophages. We developed methods for inferring networks from transcriptional data for STM virulence using several approaches. The first is to use the structure of the experiment (in this case, genetic knockouts of a number of regulators) to generate an effect network of causation between regulators. Importantly, we found that the bottlenecks in these networks (genes that restrict information flow) were more likely to be essential in virulence, providing a wealth of directly testable hypotheses. Finally, we refined our computational method for predicting secreted effector proteins that allow us to define the interface more distinctly between the pathogen and host.

We began to gather a compendium of micro-array data from public sources that catalog the response of mouse macrophages to both natural and artificial innate immunity stimulation. Individual experimental datasets were used to derive a prototype macrophage response network. We used a variety of different external data sources to provide functional information as well as to predict interactions between STM effectors and known host targets.

Proteomics Analyses of Macrophage–STM Interaction. We used global proteomics methods developed at PNNL to determine the conditions for inducing STM virulence factors and the responses of macrophage to STM infection. We identified the conditions specific for inductions of STM virulence factors important for intramacrophage survival. We also identified for the first time a group of macrophage proteins whose abundances are affected by STM infections.

In FY 2009, we will further develop our model of the host macrophage responding to infection by STM using several modeling approaches. We will extend our network topology findings to the macrophage network to identify critical nodes in the response process. Finally, we will continue to develop methods to define functional modules using available transcriptomic and proteomic data.



Relationships between genes are inferred based on shared information between their expression profiles to data from single experiments and data merged across experiments in a compendium approach that elucidated functional modules.

Mathematical/Computational Modeling of Biofilms

Andrew P. Kuprat, Paul D. Majors

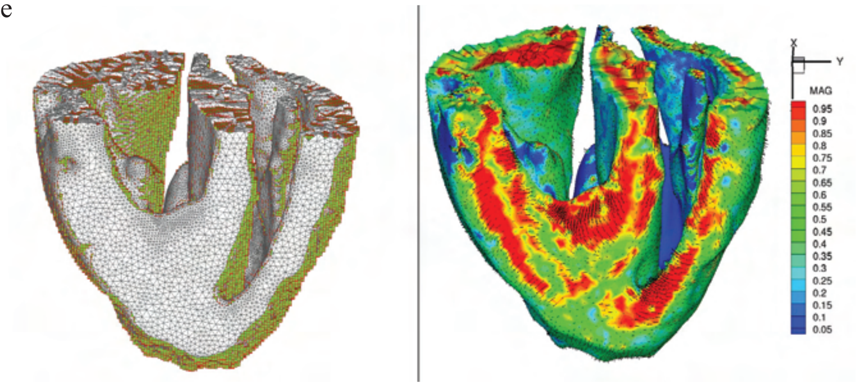
◆ This project establishes a modeling capability that can represent biofilm data in a reproducible mathematical framework. The result is more predictive science-based determination of reaction rates, transport coefficients, and a metabolic capacity for use in field-scale modeling of potential bioremediation strategies in the environment or in anti-biofilm strategies applied to the human body. ◆

Biofilms are immobile microbial colonies of enormous environmental, health, and industrial importance. These colonies can be thought of as chemical factories that can serve beneficial (remedial ecological) or detrimental (invasive biological) functions. Recently, PNNL researchers developed nuclear magnetic resonance (NMR) and combined these with optical techniques to probe live bacterial film operation. In the experimental setup, biofilms are maintained in an environmentally controlled flow chamber while using NMR to measure time- and depth-resolved metabolism and mass transport. These methods have been developed in conjunction with environmental and health-related bacterial film studies. In addition, upscaling algorithms for mapping biofilm and tissue processes onto larger field-scale computations are being developed, allowing small-scale effects to be incorporated in a science-based fashion into subsurface environmental or whole organ biomedical simulations.

An adequate understanding of biofilm operation requires a mathematical and/or computational effort to develop models that explain the experimental data. We use a synergistic combination of experimentation and mathematical/computational modeling to respond to this challenge. To achieve a quantitative understanding of biofilm systems, the interaction of multiple species and metabolites in the biofilm is best modeled as a time-dependent system of partial differential equations in one, two, or three spatial dimensions.

After modeling, the metabolism and effect on the microscopic environment of microbes in FY 2007 with AQUASIM, we focused on developing the capability of upscaling results from microscale to continuum scale simulations. Microscale phenomen, a such as microbe or cell metabolism, have an important effect on the PNNL-modeled continuum scale phenomena, including Subsurface Transport Over Multiple Phases (STOMP) simulations of bioremediation and organ-scale effects such as in cardiovascular fluid-structure simulations. In FY 2008, grid-to-grid software was adapted to mapping MRI-voxelized microscopic heart tissue data to an unstructured grid as would be required by an organ-scale fluid-structure interaction model of heart function. In the Figure, we depict the automatic mapping of cellular data. Data consists of the direction vector of the myofibers of a sheep heart as revealed by diffusion tensor MRI. On the left-hand side, we show the overlap between the microscale mesh consisting of a voxelized MRI dataset and the macroscale consisting of an unstructured finite element mesh. On the right, we show a color-coded depiction of the magnitude of the vector field mapped onto the unstructured mesh. The innovative mapping algorithm executes in O(NlogN) time, where N is the number of nonzeros in the matrix of overlap between the voxel mesh and the unstructured mesh. If necessary, the algorithm can map fields in an exactly conservative fashion or so that constants are preserved and no spurious maxima or minima are created.

Also during FY 2008, an upgrade of experimental biofilm capabilities was undertaken: development of a new third-generation PNNL confocal-NMR microscope. The new hardware is designed mainly to improve the sensitivity of measurements, the water suppression, and resulting depth profiles. The system is approaching completion, and modeling data should be available later in 2008. With continued funding, these data will be combined with modeling capabilities to yield a state-of-the-art coupling between biofilm experiment and simulation. In the meantime, the AQUASIM biofilm model developed in this project is currently being used by our collaborators.



Development of multiscale mapping technology. The left-side figure shows overlap between voxel mesh containing microscopic data of myofiber orientation in a sheep heart and unstructured mesh for organ-scale computations; the right-side figure shows magnitude of mapped myofiber vector field.

Modeling Nanoparticle-Cell Interactions

Brian D. Thrall, Justin G. Teeguarden, Harish Shankaran, Bobbie-Jo M. Webb-Robertson,
Alejandro Heredia-Langner, Roberto P. Lins, 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. We propose to develop experimental and computational approaches to describe 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 thereby influenced by both the level of receptor expression and particle surface chemistry. An understanding of these initial interactions will facilitate the rational design of safe nanomaterials in the future. ◆

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 greater than 0.5 µm macrophages has been classically associated with phagocytosis, where smaller particles are thought to use endocytic pathways using clathrin-coated pits and caveolae-rich domains. Others have suggested that particles 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 are expected to dictate cell dose (and potentially toxicity).

In this project, we are developing experimental tools and computational approaches to understand the role that specific cell surface receptors play in mediating initial interactions between nanomaterials and cells and to determine relationships between surface physio-chemical properties of nanomaterials, their cellular uptake, and subsequent biological response. Our initial focus is on scavenger receptors, which 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 large particulates (greater than 100 nm) such as SiO_2 and TiO_2 interact with macrophages through scavenger receptors. However, it is uncertain whether nanomaterials use similar mechanisms for cell entry.

To investigate this hypothesis, model cell systems are being developed where either the expression of the endogenous scavenger receptors is selectively silenced using siRNA viral transduction technologies or where new scavenger receptors are introduced. Flow cytometry along with live cell microscopy, including single molecule microscopy techniques, are used to investigate the effect of receptor manipulation on the binding and internalization of fluorescently-labeled nanomaterials bearing different surface chemistries.

Parallel to these experimental activities, we are developing statistically-based quantitative structure-activity relationship (QSAR) models to identify quantitative and predictive relationships between chemical properties and their biological effects. These models include molecular-level descriptors of particle surface physical and chemical characteristics with the ultimate goal of determining specific properties that dictate cell uptake and its relationship with cellular responses. To measure macrophage cellular responses, protein ELISA microarray analysis will be 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.

During the first year of this project, we 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 (HEK), which normally do not express SR-A1, were used to introduce SR-A1 using lentiviral transduction methods, resulting in mutant cell lines that expressed high levels of the protein on the cell surface. These efforts provided cell models where both loss and gain of function studies could be performed against identical genetic backgrounds. Flow cytometry and microscopy studies have been performed using model fluorescent nanoparticles (20-1000 nm) to investigate the effect of SR-A1 silencing or overexpression on particle uptake. 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 ~10% 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. We also conducted experiments to compare the cytokine secretion in wildtype and SR-A deficient RAW 264.7 macrophages. While these studies are ongoing, initial results suggest that the secretion of inflammatory proteins induced by nanomaterial treatment is coupled with the level of scavenger receptor expression.

Methodologies for development of QSAR models have utilized data provided through collaboration with Oregon State University investigators. An initial QSAR model has been developed that accurately describes size-dependent toxicity effects of gold nanoparticles in a zebra fish development model and has laid a foundation for applying QSAR modeling to our mammalian cell systems. In addition, we have extended this modeling approach to include molecular dynamic-based descriptors of the nanomaterial, as well as a preliminary docking model of the interaction between amorphous silica surfaces and the proximal end of the scavenger receptor. The latter model is based on published crystallographic structures obtained from Class A scavenger receptors. Our initial docking model results yield two potential primary binding sites for SiO_2 within arginine (cationic)-rich sites on the receptor dimer surface. These results lay the foundation for future experiments for determining the precise binding interactions in cells using approaches such as site-directed mutagenesis.

During FY 2009, we plan to use the previous level of information in future QSAR models that describe differences in receptor-mediated particle uptake due to differences in particle surface charge and chemistry. Ultimately, the integrated approach will provide key insights into particle surface properties that can guide safe nano design by identifying key properties that drive interactions with macrophages that determine the pro-inflammatory effects of nanomaterials.

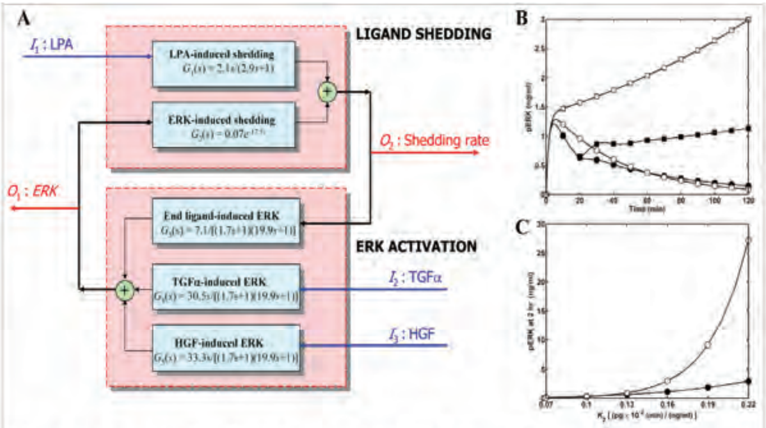
Module-Based Analysis of Autocrine and Paracrine Cell Signaling

Harish Shankaran, Haluk Resat

◆ Cells use signaling pathways to convert information about their environment into biological responses, such as growth, division, or migration. A comprehensive understanding of cell signaling can pave the way for rational therapeutic strategies for cancer. Further, modeling techniques developed as part of this project will be widely applicable to the analysis of the design principles of biological systems. ◆

Cells process information using exceedingly complex biomolecular networks involving hundreds of individual molecules. Mathematical models that include details of all individual reactions are difficult to construct and parameterize. Hence, we propose a module-based approach that involves partitioning of a cell signaling network into distinct functional parts that can be studied in isolation that will enable a hierarchical investigation. At the system level, we will employ control systems theory to quantify the input-output relationships of and the connectivity between the modules. We will also construct models that include the molecular level detail for the individual modules of the signaling network. Overall, this strategy will enable us to predict the effect of altering individual molecular reactions on the cell signaling network.

In this project, we will employ a module-based approach to predict the information flow dynamics in the epidermal growth factor receptor (EGFR) system, which involves a large number of molecular reactions and plays fundamental roles in development, tumorigenesis, responses to injury, and tissue homeostasis. Further, there is a large amount of quantitative information available about this system that makes development of mathematical models feasible. The EGFR system is capable of functioning both in a paracrine fashion, where the inputs arrive from neighboring cells and in autocrine, 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 developing comprehensive predictive models.



System-theoretic modeling of the EGFR signaling circuit. A) Block diagram for EGFR activation. The inputs to the model are the time-dependent concentrations of LPA, TGFα and HGF. The outputs are the time-dependent values of phosphorylated ERK and the ligand shedding rate respectively. Module transfer functions were determined by fitting the model to experimental data. Modules with an '*s*' in the numerator show an adaptive response, and a term of type exp(-$t_d s$) indicates that the module responds with a dead time of t_d mins. B) ERK activation dynamics in response to a unit step change in TGFα in the presence (closed markers) and absence (open markers) of a delay in ERK-induced shedding. Results are shown for two different values of the gain K_2 of the ERK-induced shedding module (G_2): $K_2 = 0.07$ (circles), and $K_2 = 0.16$ (squares). C) ERK activity at 2 hr following a unit step change in TGFα as a function of the gain in ERK-induced shedding. Results are shown in the presence (closed circles) and absence (open circles) of a delay in ERK-induced shedding. As seen, the delay increases the robustness of the system. The output amplitude becomes relatively insensitive to the feedback gain in the presence of the delay.

The EGFR network is activated in response to a variety of agonists (inputs to the cell signaling network). In order to understand the logic of this circuit, we collected experimental data for two distinct system outputs (ERK activation and ligand shedding) in response to three distinct agonists: LPA, TGFα, and HGF, each of which activates the EGFR circuit using a distinct mechanism. We used this data set to construct a coarse-grained model that enabled us to explore quantitatively the circuit design principles. We defined the system as comprising five modules that convert inputs to outputs and determined the properties of each module using system theoretic analysis. The input-output module properties were quantified in terms of transfer functions that were derived from system modules and revealed some module displays of an adaptive response, wherein a transient output is generated in response to a sustained input. Further, our analysis revealed that positive feedback from the ERK activation module to the ligand shedding module occurs with a delay of ~20 minutes.

In addition to the coarse-grained system theoretic model for the entire circuit, we developed detailed and "skeletal" differential equation-based models for the receptor activation module in the EGFR signaling network. Further, we have used a transfer-function model to quantify the relationship between receptor activation and signal transduction in the EGFR signaling network. This work has already led to two published journal articles, and a third manuscript is currently in press.

Our results so far have demonstrated the feasibility and utility of a module-based approach for understanding a complex biomolecular network. In FY 2009, we will further partition our initial coarse-grained model to understand the functioning of the receptor activation and signal transduction modules in the EGFR system. We will perform targeted experiments that will inhibit specific parts of the signaling network in order to validate the transfer functions. We will also construct a mechanistic model for the ligand shedding module. Overall, these studies will enable us to understand quantitatively how the EGFR system integrates various inputs to generate a response. We will also be able to identify specific strategies for engineering the network to elicit desired responses.

Morphological, Functional and Redox Studies of Synechocystis 6803 and Cyanothece 51135 Bacterial Membrane Complexes by Methods of Electron Microscopy

Alice C. Dohnalkova, Christina L. Bilskis, Eric A. Hill

◆ The understanding of processes occurring in photosynthetic bacteria during the light and dark cycle, including photosynthesis, carbon storage, and nitrogen fixation, presents a huge potential for the development of alternative energy technologies. This research introduces innovative methods for visualization dynamic changes in bacteria during these processes. ◆

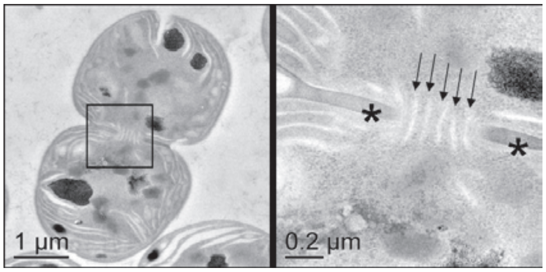
Recently, great progress has been made in obtaining genomics and proteomics data from cyano-bacteria, clearly showing periodic oscillations of certain protein expressions during the light and dark cycle. Despite the wealth of structural information available on individual proteins, much remains to be learned about protein localization, conformation, and organization in situ under native conditions in relation to thylakoid membranes.

In FY 2008, we focused on two areas: investigations of *Cyanothece* cell division with morphological change observation implications for cell function during circadian cycle and immunolocalizations of selected proteins known to be involved in CO_2 concentrating mechanism in cyanobacteria. The collaborative effort investigating *Cyanothece* division physiology involved several groups analyzing cells prepared by a precisely controlled bacterial cultivation in bioreactors. Results concluded important observations about *Cyanothece* physiology. Our group focused on monitoring formation of the cell wall septa in synchronous growth of *Cyanothece*. Cells were grown in nitrate-depleted media, and transmission electron microscopy was used for a high-resolution imaging of cell morphology with the implication on function during the cell division event. Current knowledge of cell division of Gram negative bacteria has been derived from *E. coli* studies; the intricate internal structure of cyanobacteria adds another layer of complexity to the cell division.

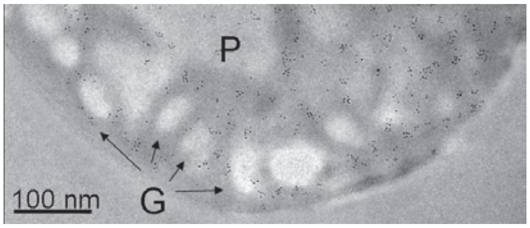
Controlled cell cultivation in a bioreactor presented a unique opportunity to study *Cyanothece* physiology in precise synchronization with their life cycle. Careful sampling during the 24-hour light and dark cycle captured the temporal cellular events with unique conclusions. *Cyanothece* cell division occurs once in 24 hours. The first physical signs of cell division occur precisely at the end of the third hour of the light cycle (L3). The formation of cell wall septa includes events of invagination of mucopeptide and cytoplasmic membrane, the exclusion of outer membrane from the septum, and formation of cell cross-wall and ingrowth of the outer membrane during cell separation, all within ~60 minutes during L4. The physical separation of thylakoid membranes that lay in the way of the newly forming septum, compartmentalization, and the final cell internal rearranging takes place within the fifth-hour light cycle; the septation stage is finished by a complete cell cleavage and separation at the beginning of the sixth-hour light cycle.

Immunocytochemistry involved the localization of *Cyanothece*'s protein complexes that play an important role in the transport of carbon across the cytoplasmic membrane during carbon fixation. Assembled from four different subunits, the CmpABCD transporter was previously characterized. If expressed and assembled at high levels under desired conditions, this protein complex has the potential to increase the efficiency of carbon uptake and cyanobacteria fixation significantly.

Cyanothece cells were grown in a bioreactor in the nitrate-limited conditions and were processed using a modified protocol for immune reaction localization in plastic sections. The epitopes of the Cmp A and B in the cell cross-sections were visualized by attachment of a secondary antibody labeled with 5-nm gold particles. The distribution of the tagged proteins showed a fairly homogeneous coverage throughout the *Cyanothece* cytoplasm during several light cycle time points. The data from other groups of a research team complement these findings.



TEM image of a dividing Cyanothece *cell; during the L4 and L5, emerging septum divides the cell and its internal material. Thylakoid membranes (arrows) will undergo physical separation in the final stage of division.*



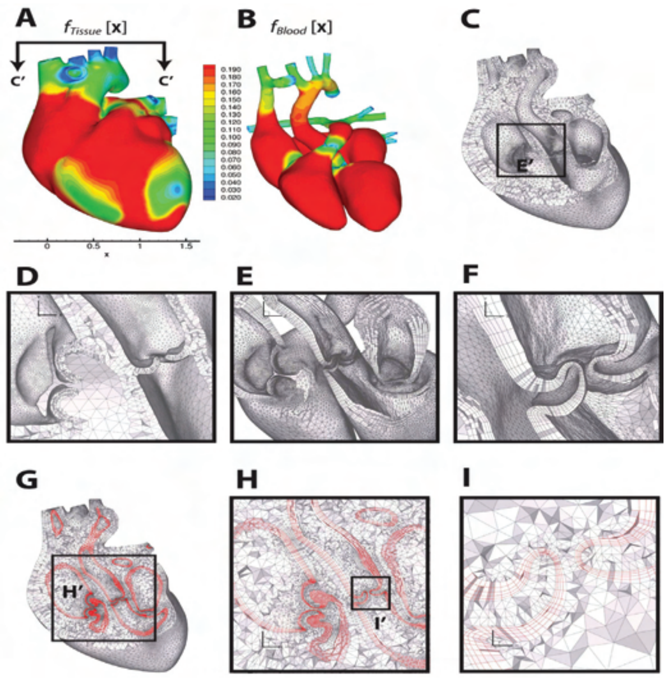
Immuno gold localization of CmpB receptors at D4. Nanogold particles tagged to the antibody against the Cmp protein complex show uniform distribution throughout the cytoplasm with void spaces where glycogen (G) and phosphate (P) granules are positioned.

Multiscale Computational Model of the Heart to Predict Airborne Particulate

Daniel R. Einstein, Andrew P. Kuprat, Kevin R. Minard, Charles Timchalk

◆ We are developing methods and capabilities for creating a multiscale computational model to investigate the relationship among atherosclerosis, the presence of nanoparticles, and the secondary perturbations of respiratory inflammation. ◆

This research was directed at generating the necessary preliminary data and computational technology to develop a multiscale computational model specifically of the murine heart to link cardiovascular to respiratory function. Computational fluid-structure interaction studies of the heart have a long but sparse history, beginning with the seminal introduction of immersed boundary methods in 1992 by Dr. Charles Peskin. Since then, no models have included the coronary circulation nor even valvular mechanics, and none has correctly resolved the interface within a Lagrangian framework. This capability is critical because it is precisely at the interface between blood and endothelium that atherogenesis occurs. These limitations have been largely technical; therefore, our goals were to overcome the most important of these through scientific innovation.



Multi-material boundary layer mesh of a human heart consisting of heart tissue, blood boundary layer, and blood domains. Panels A and B show the feature size field on the outer surface of the heart tissue domain and the blood domain, respectively. Panel B shows the feature size field on the outer surface of the blood domain, and Panel C shows a cut through the heart muscle tessellated with layered tetrahedra, where the orientation of the cut plane is indicated in Panel A. Panel D shows the detail of the layered tetrahedral mesh of the heart tissue. Panels E and F are zoomed-in views on the regions of the cardiac valves, showing the prismatic boundary layer alone. Panels G, H, and I show the prismatic boundary layer at about 25% of the gradient-limited feature size of the blood domain, sandwiched between the layered tetrahedra of the tissue and the Delaunay tetrahedra of the blood.

This research is focused on acquiring the necessary imaging data to construct a fully segmented three-dimensional computational grid of the heart and developing the necessary image processing capabilities to resolve the structures of interest. It is expected that our image processing software will be fully integrated with the National Library of Medicine-sponsored Insight Toolkit, and that we will have developed and implemented algorithms for the nonlinear registration and segmentation of disparate cardiac imaging datasets.

In FY 2006, we laid the groundwork for achieving our goals by innovating key algorithms for the efficient and accurate distillation of cardiac geometry from a magnetic resonance image, creating a parallel geometry from serial cryomicrotome data with cellular resolution and establishing a novel theoretical framework for active and passive behavior of cardiac tissues. In FY 2007, we extended some of these capabilities to domains comprised of multiple materials by 1) innovating a multi-material version of our scale-invariant tetrahedral meshing algorithm relevant to a broad class of computational problems, 2) implementing a novel multi-material marching cubes algorithm for distilling consistent interfaces from medical imaging data, 3) developing a conservative grid-to-grid mapping algorithm for cell-centered variables (to be applied to intercellular calcium and magnetic resonance diffusion tensor data but applicable to any cell-centered field), and 4) establishing an animal protocol for mice to distinguish between coronary inflammation of pulmonary and cardiovascular origin. The last of these, the murine model, is part of a general strategy for linking computation and in vivo experiments by probing the mechanism for nanoparticle-related endothelial dysfunction. Some highlights of the protocol include labeling of macrophages and relevant biochemical signals, delivery of labeled pro-inflammatory nanoparticles to the lung, monitoring particle translocation to the bloodstream, and the ability to “turn off” alveolar macrophages selectively.

In FY 2008, we enhanced our multimaterial fluid-structure interaction capable grid generation algorithms by innovating a framework for variational generation of prismatic boundary layers on biological geometries, and by creating a framework for Lagrangian multimaterial girds. In addition, we:

- created an inverse analysis of in vivo myocardium
- performed detailed segmentations of sheep heart data

- developed a novel staggered framework for Lagrangian fluid structure interaction of biofluid-structure interaction problems
- developed a scheme for dynamic adaption of Lagrangian interfaces with contact
- developed a framework for non-linear warping of grids based on non-linear transformations of high-resolution, high-contrast imaging data to low-resolution low-contrast in vivo imaging data
- developed a protocol for quantitatively monitoring translocation of magnetic nanoparticles in vivo
- developed an innovative non-linear Krylov-Newton accelerator for multiscale linkage of three-dimensional models with lower dimensional models
- submitted six journal articles.

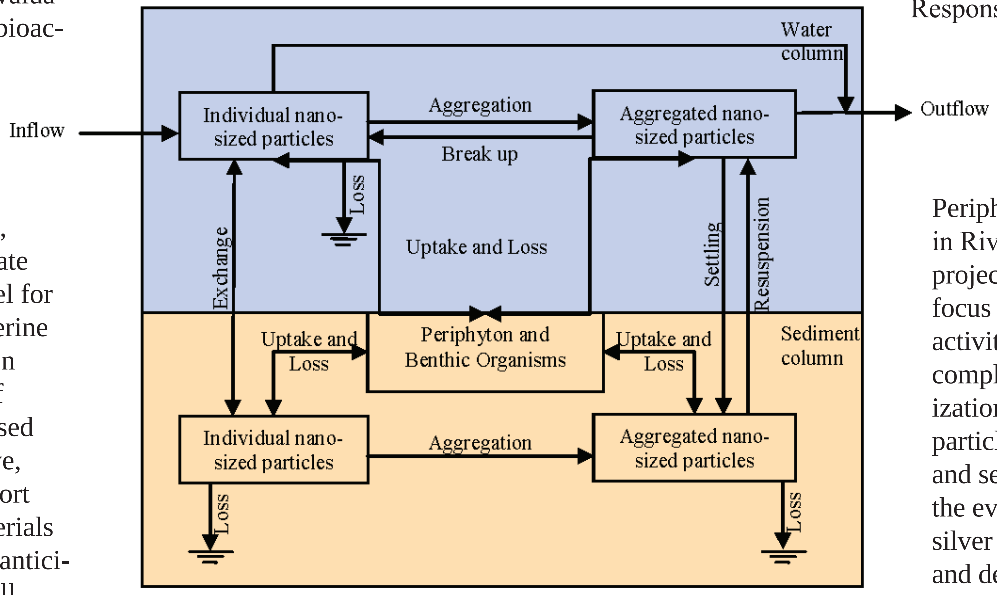
Particle-driven atherosclerosis is a multifactorial pathology. We have successfully established some of the foundational technologies for enabling the prediction of regionally specific dosage of ultrafine particulate and site selectivity of atherosclerotic plaque formation. We see this effort as an important step in the investigation and identification of the possible roles of shear stress receptors and sensitivity in acute atherosclerotic disease.

Nanomaterial Fate, Transport and Transformation in a 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 (e.g., in antimicrobial materials) or indirectly (e.g., 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. ◆

In order to build an effective, predictive, mechanistic model of the fate, transport, and transformation of nanomaterials in a freshwater environment, we are proposing to evaluate the riverine system using several approaches taken from mate arial science, analytical and colloidal chemistry, toxicology, and hydrology. Our initial conceptual model for understanding the physical, chemical, and biological processes of nanomaterials in the freshwater environment is shown in the figure below. We are evaluating the conceptual model as individual compartments using static tests and overall using flow-through bench-scale mesocosm tests. A phased approach will be used to evaluate the behavior of the silver nanoparticles in static systems, and a fresh water, bench-scale mesocosm will be used to simulate the release and transport of the nanoparticles and their interaction with biota. This approach will provide estimates of each parameter in the predictive computational model. The expected outcomes for the project are: 1) characterization of silver nanoparticles in Columbia River water and sediment, 2) evaluation of nanosilver bioaccumulation in benthic biota and changes to species diversity based on nanosilver dose, and 3) predictive fate and transport model for nanosilver in a riverine system. Information from each phase of the study will be used to build a predictive, mechanistic transport model of nanomaterials in freshwater. The anticipated outcomes will address fundamental questions about nanomaterials release into the environment and the potential risk to human and ecological health.



Initial conceptual understanding of the physical, chemical, and biological processes influencing nanoparticle fate and transport.

In FY 2008, we focused our research activities on the basic components of the conceptual design for the project. A microbial community from river sediment was examined for population biodiversity following exposure to 2 µg/ml of 30-50 nm silver nanoparticles in Columbia River water. Ribosomal intergenic spacer analysis indicated that there were shifts in the microbial community in response to the silver nanoparticles; however, the results were not significantly different from the shifts observed in response to ionic silver. This contrasted with initial exposure studies with a benthic crustacean *Hyalella azteca*, where the organisms were found to have an LC50 of 141 µg/L of 30-50 nm silver nanoparticles in Columbia River water compared with published literature values ranging from 4 to 8 µg/L of ionic silver.

In addition to biotic exposures, investigations were conducted on the size fractionation and stability of silver nanoparticles in Columbia River water. These results suggest that the nanoparticles may aggregate in Columbia River water as a function of concentration. We found that the lower the concentration of nanoparticles, the larger the particles. We theorize that this may be a function of the organic material in the river water, and these results could be significant in explaining the toxicity of silver nanoparticles compared to colloidal or ionic silver.

Continuation of this research and an expansion from related work under the "Community-Based Biomarkers of Exposure and Functional Response in the Sediment/Water Interface of the Hyporheic Zone in River Systems and Periphyton Community in River Systems" project will be the focus of our FY 2009 activities. We aim to complete the characterization of silver nanoparticles in river water and sediment, complete the evaluation of nanosilver bioaccumulation, and develop the fate and transport model for nanosilver in a riverine system.

Nanoscale Characterization of Nanomaterial-Cell Membrane Interactions

Galya Orr, David J. Panther, Kaylyn J. Cassens, Barbara J. Tarasevich, Joel G. Pounds

◆ Our research has identified physical and chemical surface properties of nanoparticles that govern mechanisms of their cellular interactions and internalization pathways. Understanding the relationships between particle properties and these cellular processes enable the assessment of nanomaterial potential toxicity or biocompatibility and aid in formulating new nanomaterial engineering and exposure guidelines. ◆

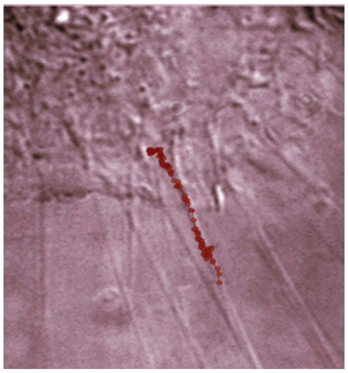
As the result of increased usage in industrial and medical applications, the environmental or occupational exposure to submicron and nanoscale materials is expected to increase within the next few years. Particles ranging from 1 nanometer (nm) to 1 micrometer that enter the respiratory tract can reach the alveoli at the distal ends of the respiratory tree where the alveolar type II epithelial cells (distinguished by apical microvilli) can be found. These cells play critical roles in alveoli function by secreting pulmonary surfactants that prevent alveolar collapse with expiration and by differentiating into type I epithelial cells to replace damaged cells. Alveolar type II epithelial cells exposed to submicron and nanoscale amorphous silica particles respond with an increase in the inflammatory gene expression and the release of chemokines.

Nanoscale particles have been shown to exert harmful effects on human health to a greater extent than other fine particles, and some of these adverse effects have been linked to the surface properties of nanomaterials. However, the specific chemical and physical parameters that facilitate nanoparticle interaction with cells and elicit inflammatory and toxic responses have not been fully characterized. Furthermore, little is known about the mechanisms that underlie the attachment and internalization of individual or a few nanoparticles or nanoscale aggregates, as they are likely to be presented to cells *in vivo*.

Using video-rate fluorescence imaging with single-molecule sensitivity, we have identified processes in this project underlying the attachment and internalization of individual nanoparticles with well-defined properties by alveolar type II epithelial cells. This approach avoids the experimentally induced agglomeration of nanoparticles and delineates the processes likely to occur *in vivo*. We have also identified specific transmembrane molecules that mediate the attachment and internalization of nanoparticles that carry positive surface charge. The studies identified relationships between nano-material properties and cellular interactions and pathways, unraveling mechanisms of nanoparticle toxicity or biocompatibility.

Particles can enter the living cell through diverse mechanisms that are strongly dependent on particle size and surface properties. Additionally, surface properties play a key role in particle toxicity. Increasing the positive surface charge by amino groups has been shown to increase particle uptake and toxicity directly. Our studies focused on the cellular interactions and internalization pathways of submicron and nanoscale precipitated amorphous silica particles, where unmodified particles have been compared with modified particles to carry positive charges on their surface.

We found that submicron and nanoscale particles are able to travel along filopodia and microvilli-like structures toward the cell body of cultured alveolar type II epithelial cells, where they can be internalized via small membrane vesicles. We discovered that this retrograde motion is strictly dependent on the positive surface charge of the particles and on the retrograde actin flow in these structures. Our observations indicate that positively charged particles bind negatively charged membrane molecules that in turn interact directly or indirectly with the actin filaments within filopodia and microvilli. As the retrograde flow of the filaments is generated in these structures, it leads to the retrograde motion of the membrane molecule and its bound particle. The retrograde pathway brings a new mechanism by which positive surface charge supports particle recruitment (and possibly subsequent toxicity) by polarized epithelial cells bearing microvilli. Looking more closely at the processes that occur at the cell body, we found that the nanoscale particles can enter the cells via clathrin-coated pits, but 500-nm particles are excluded from this internalization pathway. We also found that both 100- and 500-nm particles can enter the cells via actin-independent mechanisms. Using these clues, we identified specific membrane proteoglycans that mediate the cellular interactions and internalization pathways of positively charged particles, unraveling property dependent coupling of the particles with the intracellular environment across the cell membrane.



Positively charged amorphous silica nanoparticles scroll along microvilli of alveolar type II epithelial cell, unraveling surface property-dependent coupling of the particle with the intracellular environment across the cell membrane. Using time-lapse single-molecule fluorescence imaging, individual nanoparticles are identified and tracked from one image to the next in a time series. The trace is then plotted over the DIC image of the cell, showing the retrograde motion of the particle toward the cell body.

Noninvasive Real-Time In Situ Spectroscopic Monitoring of Macrophage-Particulate Matter Interactions to Define Biological Pathways

S. K. Sundaram, Thomas J. Weber, R. Shane Addleman, Robert J. Wiacek, Brian J. Riley

◆ This research will provide an integrated approach that combines infrared spectroscopy, dosimetry, chemical toxicology, biomarker research, and integrated optics to rapidly screen and improve the accuracy and timeliness of estimates of human risk from complex exposures to nanomaterials. ◆

The overall goal of this project is to develop a new airborne testing capability with complementary Fourier transform infrared (e.g., attenuated total reflectance) spectroscopy (ATR-FTIR) that will be useful for real-time, live-cell, in situ, deployable, high-throughput screening of cellular responses to nano-particulate matter (nPM). Specific aims are to attach viable macrophages to infrared transparent optical fibers and determine whether nPM matter-induced infrared-observable changes in macrophages can be attributed to biomarkers of the inflammatory response, including iNOS, Cox-2, and TNF-α. In following years, the measurements will be extended to study the toxicity and pathways of selected nPM. These results will provide the information necessary to evaluate the application of this new technology to nPM-related research as well as determine additional biological applications.

Our research is expected to lead to a novel capability at PNNL that can identify and discover biomarkers for multiple biological responses to a variety of stresses using infrared spectroscopy and microscopy. The high-value research capabilities associated with appropriate interfacing to imaging technologies and whole animal models will also provide additional key data that will help expansion of the current virtual respiratory tract model. We assembled a multidisciplinary team to accomplish the goal.

In FY 2005, we focused our initial efforts on demonstrating the FTIR spectroscopy proof-of-principle: the sensitivity to monitor real-time changes in the response of macrophages to endotoxin, an important component of particulate matter.

During FY 2006, we demonstrated the feasibility of using FTIR spectroscopy to track the response of macrophages to lipopolysaccharide (LPS) in real-time.

In FY 2007, we completed establishing a dedicated facility for live-cell FTIR spectroscopy for studying nanotoxicity and collected several spectra on different nano-systems. Major accomplishments included the following:

- *FTIR Spectra of RAW 264.7 Cells Treated with LPS*. LPS induces an inflammatory response in macrophages, which in turn, is associated with protein carbonyl formation. We observed an increase in a peak at wave number 1652 corresponding to carbonyl bond (C=O) in LPS-treated macrophages consistent with the inflammatory response.
- *FTIR Observable Particokinetics*. We demonstrated that FTIR can observe and quantify the settling of 1 µm silica particles with rates that tightly match predictions made using a physical particokinetic model.
- *Advanced FTIR Data Analysis*. We completed an initial evaluation of FTIR spectra using advanced statistical methods, including principal component analysis (PCA). Our results indicated that the spectra associated with endotoxin- and 10-nm silica-treated cells can be clearly resolved using PCA.
- *Importance of Adsorbed Proteins in Guiding Nanomaterial Uptake and Toxicity*. Studies with single-wall carbon nanotubes (SWCNTs) and silica nanoparticles indicate that proteins adsorbed to their surface significantly influence nanomaterial uptake and toxicity. These studies will ultimately be used to advance detailed interpretation of FTIR-observable signatures associated with nanomaterial-treated cells.

In FY 2008, we continued to test the FTIR-observable signatures that are predictive of higher-order biological processes. Major accomplishments are as follows:

- Albumin was identified as the major fetal bovine or human serum/plasma protein adsorbed onto SWCNTs, while a distinct protein adsorption profile was observed when plasma from the Nagase analbuminemic rat was used. Damaged or structurally altered albumin is rapidly cleared from systemic circulation by scavenger receptors. These results were published in *Toxicological Sciences*.
- S. K. Sundaram and Thomas J. Weber were guest editors for the recently released *International Journal of Nanotechnology* Special Issue on Nanotoxicity.

Particulate Matter Exposure and Respiratory Effects Biosignature Discovery

Justin G. Teeguarden, Lisa W. Masiello, Thomas J. Weber, Dennese M. Smith, Joel G. Pounds

◆ The purpose of this research is to develop capabilities in particulate matter, nanoparticle generation, and animal exposure. The in vitro system will also be used to test and validate a computational model of in vitro particokinetics and dosimetry, producing a novel computational tool for designing and interpreting biomarker studies for nanomaterials. ◆

Energy-generating activities such as the burning of fossil fuels by diesel- and gasoline-powered vehicles and coal- and gas-fired power plants are important sources of airborne particulates and established contributors to air quality-related health concerns (respiratory effects). Particulates from large agglomerates to micro- and nanometer scale comprise airborne particulate matter. A limited number of biomarkers of exposure and response have been developed for some environmental pollutants, but principally in tissues such as blood that require invasive sampling techniques. By creating new methods for using in vitro cell culture systems, in vivo exposures to particulates, and rapidly evolving technologies such as bioinformatics, genomics, and proteomics, this research seeks to advance the biomarker discovery field for environmental respiratory tract diseases. As nanotechnology matures, public and scientific communities are becoming increasingly aware of the need to determine nanomaterial characteristics. With improved understanding, product development, and regulation, we can safeguard human and ecological health while ensuring U.S. competitiveness in the global market.

Additional biomarkers with strong linkages to the underlying disease process are needed to advance the biomarker discovery field for environmental respiratory tract diseases. This research aims to develop core capabilities in engineered nanomaterial generation and animal exposure and to use this capability to: 1) generate respiratory tract tissue and fluid samples suitable for "omics"-driven biosignature discovery, 2) conduct a combination of proteomic and biochemical (tumor necrosis factor-alpha, malondialdehyde) analyses on bronchio-alveolar and nasal lavage fluids as well as exhaled breath condensate, and 3) identify a biosignature of nanoparticulate matter-induced respiratory effects from these data. An affiliated objective is to develop a corresponding high-throughput in vitro system for identifying biosignatures of epithelial cell and macrophage response to engineered nanomaterial. We expect to identify a biosignature of nanomaterials-induced respiratory effects to be testable in humans that will generate important mechanistic data used to realize the predictive value of an available virtual respiratory tract model.

Proteomic and genomic studies conducted in 2006 and 2007 identified several important viable biosignature candidates for measuring pulmonary response to inhaled nanomaterials. To test these biomarkers and extend our discovery efforts, we conducted a rodent nanomaterial exposure study to generate lung and lung fluid samples suitable for "omic"-driven biosignature discovery. Rodents were exposed to multi-walled carbon nanotubes and separately to asbestos. This study enabled the first biosignature discovery effort that integrates conventional toxicology endpoints, with the proteomics and genomics assessment conducted at PNNL using PNNL-developed capabilities. These unusually rich data were used in 2008 to identify new material-specific biomarkers of nanomaterials exposure.

Also in 2008, we completed the development and revision of a computational model describing settling and diffusion of nanoparticles in cell culture. Critical to completing the model, confocal microscopy was used to measure settling of particles in solution, allowing validation of the model. Previously ignored, the process of simulating the solution kinetics of nanoparticles is of tremendous importance to nanomaterial toxicity screening studies typically conducted in cell culture systems. The computational tool is helping to reshape the way experimentalists conduct and interpret toxicological assessments of engineered nanomaterials and, more generally, particulate matter. This project is developing important tools for monitoring and mitigating the effects of exposure to environmental pollutants on humans.

The research conducted under this project established a new laboratory capability in particulate generation/exposure, which is central to PNNL's particulate matter research. The products of this research were used to develop and present a continuing education course in March 2008 at the annual Society of Toxicology meeting in Seattle, WA. The course advanced the sciences related to risk assessment of nanomaterials. In addition, the research team led the development of a separate symposium at the same meeting on the systemic kinetics of nanomaterials, ultimately urging the effective integration and computational sciences demonstrated in this research program.

PCR Arrays for Quantitative Evaluation of Microbial Communities

George T. Bonheyo, Jim 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, which has prevented scientists from understanding accurately or predicting environmental-scale biogeochemistry.

We are developing a unique capability that will allow the collection of accurate census data for an unlimited number of microbial (bacterial, fungal, archaeal, or protozoan) species. Phase 1 of the project will create a comprehensive list of species inhabiting (Hanford 100N and 300 Area) sediments with supporting discriminatory DNA sequence information for each species. A small number of species determined to be unique to Columbia River water (used in some remediation treatments) will also be identified. The DNA sequence data will be used to develop census-profiling kits (PCR arrays). During Phase 2, the census tools will be applied to both laboratory simulations and ongoing field-scale remediation programs to measure how microbial populations increase or decrease during treatments. These values will help identify key reactive species and allow researchers to begin translating bench-scale analyses of single cell biochemical rates to environmental community scale process models.

This project will generate methods and data needed to enable quantitative field-scale measurement and modeling capabilities of subsurface microbial communities in the Hanford area. These measurements require development of a new capability for collecting microbial census data. Once developed, arrays will allow for rapid (less than 8-hr sample extraction through data output) comparisons of control and test communities. The proposed capability is both enumerative and fully scalable for complex environments.

The experimental process will follow six steps over the length of the project: 1) collection of samples and extraction of nucleic acid, 2) PCR amplification, cloning, sequencing, and species identification/OTU definition, 3) sequence alignments, primer design, testing of arrays, and preliminary data visualization training, 4) backtest arrays against original samples, 5) run case study experiments and analyze new samples using the primer arrays, and 6) data visualization and integration with other data sets. At all stages, available literature and DNA databases will be used to supplement primer designs.

The project began in July 2008. Over 125 sediment and well (pore) water samples were acquired from the Hanford 100N and 300 Area and from laboratory simulated injection studies. Each sample has been processed to extract total community genomic DNA; next, the samples were divided into three fractions, each undergoing a different method of extraction. One was subjected to a combination of chemical and thermal lysis, the second underwent mechanical lysis using bead beating, and the third was processed using a commercially available kit. 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.

Following development, census tools will be used to profile the archived extractions and evaluate expected biases of each method. Two-thirds of each composite DNA specimen will be archived; the remaining third derived from similar environments will be pooled to create a composite DNA profile for that environment. These composites will be used for PCR amplification of species identifier genes. Concurrent with DNA preparations, existing literature was reviewed to evaluate published PCR primer sequences flanking the discriminatory target sequences. Additional primers were designed based on sequence alignments made using representative sequences of all major divisions of eubacteria and two representative Archaea.

PCR amplifications will continue into FY 2009 using multiple primer sets and amplification conditions to minimize biases. Amplicates will be pooled, cloned, and sequenced to identify species. The result will be a list of species found in the environments sampled. The sequences will be used to design discriminatory primers selective for a single species. A comprehensive testing regime will be used to confirm specificity, normalize amplification biases, and normalize against extraction biases. Finally, primers will be assembled into quantitative PCR kits that will evaluate the archived samples and samples collect prior to, during, and following remediation treatments and in laboratory simulations. Key questions are expected to be answered regarding microbial transport in the subsurface, identifying patterns of successive colonization, and identifying population growth patterns well-correlated with treatments.

Protein and Peptide Markers of Infection

David S. Wunschel, Heather A. Colburn, Kathryn C. Antolick, Susan M. Varnum, Kristin H. Jarman, Nathaniel Beagley, Bobbie-Jo M. Webb-Robertson

◆ Protein and peptide markers have long been recognized as having utility in determining a biological response; hence, discovery of these biomarkers offers an opportunity to detect, triage, and treat exposed and/or infected people and animals. Further, determining the response to infectious agents potentially allows for rapid threat characterization of new isolates and countermeasures. ◆

Detecting the response to infection is vital to biodefense for recognizing infection prior to the appearance of symptoms, particularly aerosol exposure. Presently, animal models serve as the testing ground for infectious disease in humans until in vitro systems using human cell types can satisfactorily replicate a human molecular response. In the case of aerosol exposure, an animal such as the C57 mouse is a common model. Using this test, aerosol exposures of mice were performed with the pathogen *Francisella novicida* in collaboration with University of Washington (UW) Medical School colleagues with a history of working with this pathogen and exposure system. *F. novicida* species are non-pathogenic to humans but are relatives of the bioweapon agent *F. tularensis*, a causative agent of tularemia, sometimes called rabbit fever.

This project applied semi-selective methods to target classes of protein and peptide markers of infection in a model system such as *Francisella* sp. The goal was to determine the protein signature related to infection, relative to uninfected controls. A mouse respiratory infection model was used to examine the small protein biomarkers of response. An experimental design was developed to randomize the exposure of the animals to the *F. novicida* mouse pathogen as well as a non-pathogenic attenuated strain of *F. novicida* and an alternative pathogen *Pseudomonas auriginosa*.

Samples of mouse bronchial alveolar lavage fluid (BALF) were collected after exposure (at the UW) and transferred to PNNL. The same blocking and randomization scheme used for exposure was applied to sample preparation for mass spectral analysis. Based on FY 2007 work, we applied the acid extraction method of protein/peptide extraction using strong cation exchange and hydrophobicity-based purification of small, intact proteins. Alternatively, a total protein precipitation and global proteomic analysis were performed to compare the detected peptides.

General protein and peptide marker discovery in animal models of disease are often complicated because there are few fully sequenced and annotated genomes. Global approaches to protein identification may also overlook informative low abundance markers or protein processing events. Therefore, we applied complimentary methods for protein discovery. The first detects and tracks protein markers in the absence of sequence information and prior to protein identification using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) alone (one-dimensional data sets) or after high-pressure liquid chromatography (HPLC; two-dimensional data sets) to generate mass spectral patterns of proteins and peptides in each sample. A second proteomics detection method was used to provide a complimentary method for detecting proteins, which involved protein precipitation and proteolytic digestion to create peptide markers identified using electrospray ionization (ESI) and tandem mass spectrometry (MS-MS). Data from both approaches were statistically analyzed to find significant markers.

Protein marker discovery used a statistical marker comparison based on a Kruskal-Wallis test to extract the relevant peaks using the MatLab® Version R2008a. The Kruskal-Wallis test is a nonparametric version of one-way analysis of variance, which tests the hypothesis that samples are drawn from the same population. The test will return a significant p-value if any one of the defined groups has a normalized average peak area over the replicates that is significantly different from the rest. Our results demonstrated that there are identifiable differences in secreted protein/peptide patterns between mouse BALF samples exposed to *F. novicida* and less pathogenic *Pseudomonas* and nonpathogenic *F. novicida* strains. Samples from each category could be correctly identified 75% of the time by MALDI-MS and 83% by global proteomic analysis alone.

In FY 2008, the data on protein markers of exposure were combined with data from metabolite analysis performed using nuclear magnetic resonance. The goal was to determine if the sets of markers detected by each technique could be successfully integrated to differentiate between samples from each type of exposure. The BALF samples could be correctly classified 89% of the time using this integrated approach, which indicated that responses from the exposed mice were distinguishable from unexposed mice or those exposed to alternative pathogens.

Our results demonstrate the application of both a MALDI-MS and ESI-MS-MS analytical approach for protein marker extraction, visualization, and comparison. These techniques were effective tools in discriminating marker sets from different types of exposures. Most importantly, the integration of these data sets with other data streams was the most effective approach for exposure identification.

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

Tao Liu, Bobbie-Jo M. Webb-Robertson

◆ Nanomaterials offer many new, interesting developments in biomedicine and technology; however, relatively little is known about their potential biological risks. This project is designed to understand the relationship between differential protein binding and surface nanomaterial properties. This study will allow us to create computational models that permit predicting protein binding to and provide general insights 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, much of the previous work on protein adsorption to particles has focused on isolated individual proteins or simple mixtures or has only been able to analyze 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 on 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 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 employ a dual quantitation strategy (^{18}O labeling and label free) to measure accurately the differential and dynamic binding of proteins in biofluid to nanomaterials in a time course setting. Quantitative structure activity relationship (QSAR) modeling will then be employed to formalize the physical-chemical and surface properties of nanomaterials that determine the initial interaction of nanomaterials with proteins in biofluid. We will provide the most comprehensive and accurate analysis of differential protein binding of nanomaterials in human plasma to date and create powerful models that permit predicting protein binding to nanomaterials in vivo.

Important progress was made in spite of the late start during the fiscal year (July). We initially optimized proteomics protocols for the isolation and quantitative analysis of nanoparticle-associated proteins. A central methodological problem for studying nanoparticle-associated proteins (NAPs) is to separate free proteins from those bound to nanoparticles, ideally employing non-perturbing methods that do not disrupt the protein-particle complex or induce additional protein binding, followed by a second step to desorb and recover NAPs from the nanoparticle surfaces. We have thus far determined that the protein-nanoparticle complexes can be isolated effectively and rapidly by centrifugation and repeated washing, fulfilling the requirements for a temporal study using 5- and 15-minute and 1- and 5-hour time points. We also determined that the best path forward for recovering NAPs for subsequent proteomics analysis consists of sonication (in 1% sodium dodecyl sulphate), acetone precipitation, and trypsin digestion in trifluoroethanol solution, as it was reproducible, had high recovery, and was fully compatible with ^{18}O labeling for quantitative measurements.

In FY 2009, we will apply refined approaches for the isolation of NAPs, initially demonstrate quantitative proteomics strategies for time course analysis of 3 to 5 different nanomaterials, and develop and test QSAR modeling using the initial quantitative proteomics data. The experiments will be scaled up following the initial demonstration. The goal is to perform large-scale quantitative proteomics analysis of NAPs isolated from in vitro exposure of 20 to 30 different nanomaterials and refine QSAR modeling by utilizing the comprehensive quantitative proteomics data. The approach will be to apply linear and nonlinear (where necessary) regression or statistical machine learning QSAR methods to this data matrix. We will use feature extraction methods to evaluate the descriptor space and identify the subset associated with the response. In addition, the machine learning SVM approach will be employed with multiple data transformations to determine any possible non-linear relationships in the data. The product of the QSAR modeling effort will be a final mathematical relationship between particle characteristics and qualitative and quantitative protein binding. Further, these results will contribute to the mechanistic understanding of the physiochemical properties of nanomaterials that determine cell response and toxicity and biokinetics.

Quantitative Characterization of Post-Translational Protein Modifications Using Mass Spectrometry

Wei-Jun Qian, Lee K. Opresko, Tyler H. Heibeck

◆ This project focused on the development and application of novel technologies for more sensitive and comprehensive characterization of post-translational protein modifications, gaining insight into cell signaling networks by quantitative measuring of tyrosine phosphorylation. ◆

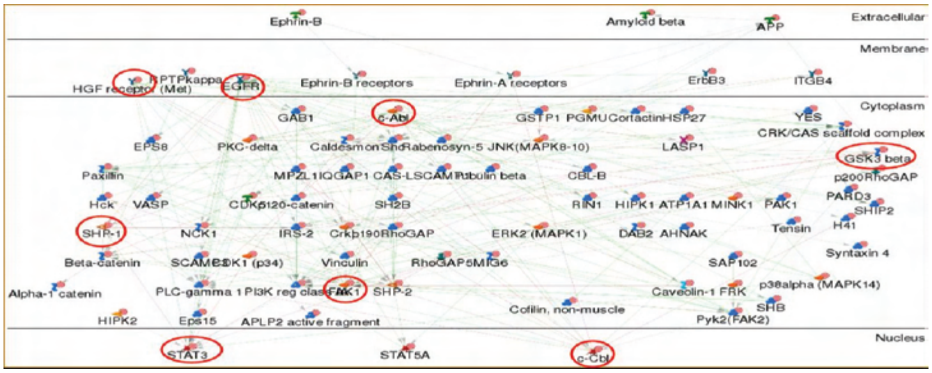
Protein phosphorylation is a central mechanism that regulates nearly every aspect of cellular life and touches almost every known signaling pathway. Oxidative modifications such as tyrosine nitration have been linked to human diseases, including cancer; radiation damage; neurodegenerative, heart, and coronary artery diseases; and normal aging. Our understanding of signaling networks and cellular functions will be significantly enhanced by the development of robust quantitative techniques that allow comprehensive and quantitative mapping of protein phosphorylation and protein-oxidative modifications.

Under this project, we have successfully developed innovative techniques for enabling global characterization of tyrosine phosphorylation and tyrosine nitration in endogenous biological samples. We demonstrated an integrated approach coupling peptide-level immunoprecipitation with high sensitive metal-free liquid chromatography-mass spectroscopy (LC-MS) platform for identifying extremely low-abundance site-specific tyrosine phosphorylation in whole cell lysates. This approach has been successfully applied to the study of epidermal growth factor receptor signaling pathways by comparative analyses of tyrosine phosphorylation. For the detection of endogenous nitrotyrosines, we demonstrated both a global two-dimensional LC-tandem MS (MS/MS) approach and a novel chemical-enrichment approach for specifically isolating nitrotyrosine peptides from complex mixtures. Significant progress has been made during FY 2008 for applying these approaches to study cell signaling pathways and for identifying novel functional important protein modifications.

Study cell signaling pathways by phosphotyrosine profiling. We have established a robust platform for quantitative analysis of site-site-specific tyrosine phosphorylation by integrating phosphotyrosine-specific antibody based immunoprecipitation applied at the peptide level and high-resolution LC-MS/MS platform. The technology has been applied to study cell signaling pathways in human mammary epithelial cells by comparatively analyzing tyrosine phosphorylation with different treatments, including simulation with insulin growth factor-I, epidermal growth factor (EGF), a chronic released ligand T-cell target, a monoclonal antibody 225 that binds to EGF receptor, and a hepatocyte growth factor. We have been able to quantify the phosphorylation differences for 531 different tyrosine phosphorylation sites among these unique conditions, which represents the greatest coverage of tyrosine sites in a mammalian proteome. The figure shows the interaction network of the quantified phosphortyrosine proteins with coverage on the EGF receptor signaling next-work. The results obtained revealed important insights related to the EGF receptor signaling networks and illustrated the powerful of such an analytical approach in systems biology studies.

Analysis of novel oxidative modification markers. We recently discovered several novel prevalent oxidative modifications resulting from free hydroxyl radicals, including tyrosine oxidation products L-dopa and L-dopaquinone and proline oxidation. In a mouse heart tissue sample, we confidently identified 113 unique L-dopa modified peptides, 80 L-dopaquinone modified peptides, and nearly 300 proline oxidated peptides. These peptides and proteins could serve as potential markers for inflammatory response and oxidative stress.

Currently, we are applying external funding from the National Institutes of Health for application projects utilizing these technologies in the areas of systems biology and biomarker discovery. We believe that these new capabilities will expand our business opportunities in the long term.



Interaction network of detected and quantified phosphotyrosine proteins show increased tyrosine phosphorylation following EGF or TCT stimulation as analyzed by GeneGo MetaCore. The network clearly illustrates some key protein interaction nodes such as EGFR, HGFR, FAK1, GSK3 beta, SHP-1, STAT3, c-abl, c-Cbl that involved in the EGFR pathways. The symbols of proteins indicate different functional classes.

Regulation of Cell Surface Ligand Dynamics

H. Steven Wiley, Lee K. Opresko

◆ Cells respond to stress by releasing bioactive proteins that affect both the releasing cell and neighboring tissues. This project is designed to understand this process so that we can detect the effects of stress early and modify some of its negative consequences. This study will improve our basic understanding of the epidermal growth factor receptor system regulation in normal epithelium and will help identify mechanisms whose dysregulation may be associated with cell damage and disease. Moreover, our findings will provide general insights into how other membrane-associated growth factor systems can regulate cell-to-cell interactions. ◆

Cells respond to stress by shedding a variety of biologically active proteins such as proteases and growth factors. In the case of mammary epithelial cells, at least four distinct ligands for the epidermal growth factor receptor are shed in response to cell stress. We hypothesized that the shedding is part of a mechanism by which cells actively interrogate their environment following a physical or biological insult. We built a quantitative model of this process using engineered cells that express a variety of different artificial and natural ligands. We found that different epidermal growth factor receptor ligands have distinct biological activities conferred by the domains flanking the core receptor-binding domain.

Under this project, we are examining the biological effects of soluble (autocrine/paracrine) ligands and the mechanisms that regulate their release and rebinding by cells. To accomplish this, we have developed a set of new imaging technologies that can directly visualize live cell response to receptor activation, thus allowing the interactive manipulation of the autocrine pathway. In addition, we developed approaches to change ligand domains rapidly and evaluate multiple nodes in cellular signaling networks. We have used the information derived from our studies in conjunction with computational modeling to gain insights about the complexities of ligand regulation and to extrapolate our results to the physiologically relevant context of tissues.

During FY 2008, we made substantial progress on this project as described below.

Pathway Delineation. We found that the PI3K, *src*, and extracellular regulated kinase pathways were critical for ligand release, implying the existence of recursive positive feedback loops in autocrine ligand production. Further experiments showed that activation of the extracellular regulated kinase (ERK) was crucial for long-term stimulation of autocrine signaling. Multiple cell signaling pathways are apparently integrated either directly at the level of ligand shedding or at the level of ERK. Furthermore, we found that although direct stimulation of shedding could be fast (<5 minutes), ERK-stimulated shedding was slow (>20 minutes). This was a very novel finding and indicates that ERK works indirectly by altering the distribution of components needed for the shedding response. Further work focused on establishing the mechanisms by which multiple signaling pathways feed into the central ERK-autocrine axis.

Extracellular Regulated Kinase Oscillations. We found that ERK was an excellent readout of cell signaling activated by induced ligand shedding. To extend our studies to the individual cellular level, we developed an image-based assay for extracellular regulated kinase activation, exploiting its translocation into the nucleus as a consequence of activation. We developed quantitative image analysis approaches for analyzing these oscillations and then developed a quantitative model of this process. We then extended our model to include several different scenarios regarding the mechanisms of ERK oscillation and used waveform analysis and signal modulation to test these models. We found that the observed independence of oscillation wavelength from signal strength is primarily due to the coupling of the ERK amplification cascade to its negative feedback loop. Previously, wavelength independence was thought to be a simple function of feedback, but our analysis shows that the amplification step itself tends to lock in the frequency range. We are exploring the significance of these findings to cellular responses.

Modular Model of Shedding Pathway. By combining our data at a functional instead of a purely biochemical level, we were able to reduce the complexity of these pathways and model them as the interaction between three functional modules. This approach greatly simplified our experiments and enhanced our ability to understand the data. We successfully created a novel transfer function-based model of the autocrine "circuit" and showed that it accurately reproduces system behavior. We then used this model to explore the design principles of this cellular circuit.

Cells Overexpressing All of the Native Ligands. We created a series of cell lines overexpressing all of the native ligands: tumor necrosis factor alpha (TGF-α), amphiregulin, heparin-binding (HB)-epidermal growth factor (EGF), and epiregulin. We found that expression of either TGF-α or epiregulin greatly accelerated cell growth. However, amphiregulin and HB-EGF expression had little effect. Further studies suggested that it was not possible to increase significantly the expression of either amphiregulin or HB-EGF over basal levels using retroviral vectors. This suggests that there are regulatory systems in cells that normally serve to keep the expression of certain ligands within a confined range. To circumvent this technical limitation so that our autocrine models can be explored further, we transferred native ligands into adenovirus expression vectors. We have been previously successful in using adenovirus to express transiently high levels of ligands in our cell type. All the ligands have been successfully transferred to adenovirus, and the testing of these vectors is underway.

Future Plans. The work over the past three years has created a strong conceptual and technical foundation for exploring the autocrine circuit in normal cells. Several papers describing this work have been submitted or are in the final stages of preparation. We plan to combine additional molecular-level studies with our modeling efforts, particularly proteomics data. Several grant proposals to continue this work are in preparation for submission over the next year.

Rfr-Domain Protein Family Characterization in Cyanothece 51142

Garry W. Buchko, Anthony Addlagatta, Howard Robinson (BNL)

◆ Understanding the biology and ecology of microorganisms is of central importance to DOE's bioremediation, neutral energy production, and carbon sequestration efforts. X-ray diffraction (XRD) crystallography and nuclear magnetic resonance (NMR) spectroscopy are being used to solve structures of proteins that may play important biochemical roles in the unique cyanobacterium *Cyanothece*, which not only sequesters carbon from the atmosphere during the daytime but also produces hydrogen while fixing nitrogen at night. ◆

PNNL is employing a systems biology approach to study the influence of environmental conditions on the unicellular cyanobacteria *Cyanothece 51142,* a microbe that could provide a potentially powerful solution to carbon-neutral energy production and carbon sequestration. *Cyanothece* is being studied because it is the simplest organism that uses circadian rhythms to perform photosynthesis during the day (carbon-sequestration) and nitrogen fixation at night (hydrogen production).

From evidence provided by classical systems biology data (genomics, transcriptomics, and proteomics), these proteins are believed to be important and fall into two groups: pentapeptide repeat (PRP, or reapted-five residue [Rfr]) proteins and proteins associated with nitrogen fixation. The first group were targeted because they are thought to be located in every cellular compartment, including membranes. *Cyanothece 51142* contains 35 Rfr-proteins that have signature protein sequences, a minimum of eight tandem pentapeptide repeats of the general consensus sequence A[D/N]LXX. Sequence analyses suggest that these 35 proteins are present in disparate cellular locations, arguing for an important physiological function. Using XRD methods at Brookhaven National Laboratory, the structure for two pentapeptide repeat proteins in *Cyanothece* were determined: cce_1272 (Rfr32) and cce_4529 (Rfr23). The tandem pentapeptide repeats fold into a right-handed quadrilateral β-helix or Rfr-fold with four distinct faces that take on the shape of a "protein skyscraper," where four consecutive pentapeptide repeats define a coil (floor) in the skyscraper, with a single repeat occupying a face. The Rfr-fold in cce_1272 contains five complete stacked ascending coils that complete a revolution every 20 residues with an approximately 4.8 Å rise along the helix axis. Cce_4529 contains four complete stacked ascending coils: two partial coils with a disordered loop protruding from one coil. Such disordered loops are often the site of biochemical activity, becoming "structured" only in the presence of the protein's biological substrate. One immediate outcome was the recognition of two distinct types of four-residue turns adopted by the pentapeptide repeats in the Rfr-fold. Labeled Type II and IV β-turns, these may be universal motifs that shape the Rfr-fold in all PRPs.

The second group of proteins is associated with nitrogen fixation, the major activity that occurs within *Cyanothece* in the dark cycle. To fix nitrogen from the atmosphere, the *Cyanothece* genome contains 34 genes in the nitrogen fixation transcriptional regulon. Analysis of transcriptomics data shows that most of these 34 genes are expressed in unison with the diurnal cycles. Of the 34, the function of 16 of these gene products is unknown, including two that fall into Domains of Unknown Function (DUF683 and DUF269) families. No structural information exists for any proteins in either of these two DUF families. We were successful in growing diffraction quality crystals of cce_0567 (DUF683) and cce_0566 (DUF269).

While analysis of the XRD data for cce_0566 is still in progress, we have determined the first crystal structure for a protein in the DUF683 family to 1.84 Å resolution. Interestingly, x-ray diffraction data collected at BNL could only be interpreted using data collected on crystals grown in the presence of Ni^{2+}. Cce_0567 crystallized in space group $P2_1$, with two protein molecules and one Ni^{2+} cation per asymmetric unit. The protein is composed of two α-helices from residues P11 to G41 (α1) and L49-E74 (α2), with the second α-helix containing a short 3_{10}-helix (Y46-N48). A four-residue linker (L42-D45) between the helices allows them to form an anti-parallel bundle that cross over each other towards their termini. In solution, two molecules of cce_0567 form a rod-like dimer by the stacking interactions of ~1/2 of the protein. Histidine-36 is highly conserved in all known DUF683 proteins, and the N2 nitrogen of the H36 side chain of each molecule in the dimer coordinate with Ni^{2+} in the crystal structure.

Using NMR spectroscopy methods, the divalent cation Ni^{2+} was titrated into ^{15}N-labelled cce_0567, and chemical shift perturbations were observed only in the ^{1}H-^{15}N HSQC spectra for residues at or near the site of Ni^{2+} binding observed in the crystal structure to confirm the binding of nickel in solution. Upon binding Ni^{2+}, there was no evidence for an increase in the size of cce_0567 even in large molar excess of Ni^{2+}, indicating that a metal was not required for dimer formation. Circular dichroism spectroscopy studies indicated that cce_0567 was extremely robust with a melting temperature of ~62ºC that was reversible. The function for cce_0567 is still under investigation; however, our structural insights provided some valuable clues as to its potential role in nitrogen fixation. Many of the nif proteins involved in nitrogen fixation contain metals, but these are Fe, Mo, and S, not nickel. However, uptake hydrogenases that contain nickel are often associated with nitrogenases in cyanobacteria; therefore, if nickel is the biologically relative metal substrate for cce_0567, perhaps it is somehow associated with the uptake hydrogenases.

Secretome Analysis of Nanomaterial Induced Biomarkers

Jon M. Jacobs, Brian D. Thrall

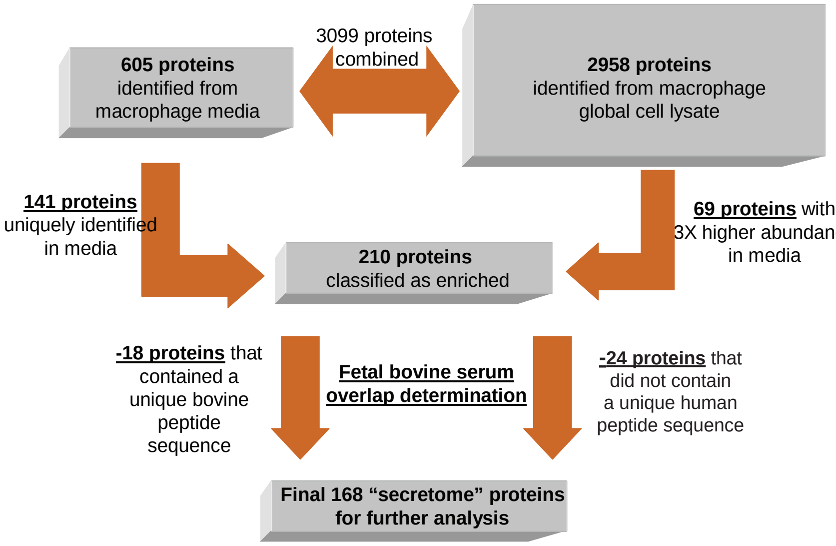
◆ Relatively little is known about the biological effects of nanoparticles. Under this project, we are developing quantitative proteomic approaches that can be applied to investigating the biological effects of exposure to particulates, including nanoparticle exposure. ◆

The study of the biological effects of nanoparticle exposures can provide important insights into both the molecular pathways affected by these particles, as well as linking potentially harmful effects to specific sizes and types of nanoparticles. A national goal for the National Nanotechnology Initiative is to develop specific biological markers of potential human health effects based upon findings from cellular and animal studies. Under this project, we tested the hypothesis that differences in specific cell signaling pathways stimulated by different types or sizes of nanoparticles in macrophages will be reflected by differences in the pattern of proteins secreted from the cell (i.e., potential biomarkers). We propose to develop approaches to measure globally both the abundance and turnover of proteins released from macrophages into the extracellular space in response to nanoparticle exposure using stable isotope-labeled amino acids to label selectively newly synthesized proteins secreted from macrophages.

Previously, we sampled the extracellular protein components (secretome) of treated macrophage cell cultures using the liquid chromatography-mass spectrometry capabilities (developed at PNNL) for global proteomic measurements. Specifically, we developed mass spectrometry-based methods and initial databases for the identification and quantification of proteins secreted or shed in response to nanoparticle and other treatments using the RAW264.7 macrophage cell line as a model system. We also performed comparative analysis between different nanoparticle treatments to elucidate differences in protein secretion patterns between different types and sizes of nanoparticle for the identification of potentially specific response biomarkers.

Our specific efforts during FY 2008 were limited to working with the previously generated secretome data both qualitative and quantitative results to further data analysis and publication. With regard to characterization of the macrophage treatment secretome database, the figure shows a schematic breakdown of the methodology developed to determine the identification of secretome-based peptides/proteins from the data. This is similar to an approach used in a previous publication we co-authored that helps distinguish protein identification from contaminant media components, cellular debris, and actual shed/secreted protein products from the cell. We are still in the manuscript phase for publishing these initial studies, which describes the first in-depth proteomic characterization of the secreted proteins from macrophages.

Additionally, the follow-up expansion of these initial experiments involved quantitative liquid chromatography-mass spectrometry studies performed to measure the effects of cellular activation and secretion upon exposure to varying particles, sizes, and doses. In total, 27 different culture treatments were used based on particles most utilized in previous studies and of most importance to DOE (particulates from energy production, nanotechnology). These included 10- to 300-nm silica particles, single-walled carbon nanotubes, and multi-walled carbon nanotubes, all at varying exposure doses. Specifically, we clearly observed cytotoxicity effects directly linked to dosing of the various particulate exposures as well as secretion of specific extracellular effectors (i.e., tumor necrosis factor-alpha, vascular endothelial growth factor, RANTES) that directly mirror previous orthogonal results and form the design basis of biomarker assays for additional studies to be performed in vivo.



Schematic of data filtering used for determining secretome proteins in the RAW264.7 macrophage cell line. The 605 proteins identified via proteomic analysis were compared with previous macrophage-based global cell lysate results, providing a subset of 210 classified as enriched in the extracellular compartment. Additional filtering was conducted with the bovine database to remove potential carryover proteins arising from bovine serum used in cell culture, resulting in a final subset of 168 secretome proteins.

Sensitive Detection of Biological Stress Response

Diana J. Bigelow

◆ This work sought to gain new insight into cellular stress responses based on the use of high-resolution global proteomics methods that measure both quantitative changes in protein abundances and stress-specific post-translational modifications. This project will lead to the development of robust approaches for quantitative analysis of oxidative modifications. The sensitive detection and understanding of biological stress response in bacteria and mammalian cells is fundamental to the DOE-sponsored program goals of both the Genomes to Life and Low-Dose Radiation programs sponsored by DOE. ◆

Sensitive, specific markers of biological stress response are essential for detecting human exposure to environmental hazards and the early detection of response progression to disease states. The universal involvement of reactive oxygen and nitrogen species generation in biological stress responses provides stable oxidative modifications of cellular proteins as biomarkers. The goal of this project is to develop and demonstrate our capabilities for reliable, quantitative, and sensitive detection of biological stress response from these biomarkers. Our approach involves analysis of global proteomic data sets obtained from several terminally differentiated mammalian tissues under physiological conditions that correspond to basal conditions. Specifically, we aim to 1) establish protein signatures of endogenous oxidative stress in tissues (brain, heart, and skeletal muscle) with varying levels of physiological oxidative stress, 2) develop tools for single molecule detection in living cells as functional consequences of oxidative modifications, 3) identify protein signatures of chronic oxidative stress associated with healthy aging and in the pathologies such as neuro-degeneration, and 4) optimize proteomic sample workup methods to prevent nitrotyrosine reduction.

Endogenous Oxidative Stress Markers. Under this project, we completed analysis of endogenous oxidative stress markers in the heart and skeletal muscle that demonstrated a preferential modification from two oxidative markers of proteins (nitrotyrosine and methionine sulfoxide) of proteins within mitochondria and structurally coupled regions of the cytoskeleton and sarcoplasmic reticulum. Such modifications provide a cellular signature of the oxidant peroxynitrite generated from nitric oxide and superoxide, which is consistent with mitochondria as the major source of superoxide in the resting cell. We expect that the identification of cellular patterns of oxidative modification will provide signatures of specific cellular oxidants, allowing us to detect if these differ in pathology or stress conditions suggested in literature. Moreover, based on our data, the endogenous modification of proteins involved in mitochondrial oxidative phosphorylation, lipid metabolism, and the unfolded protein response pathway rationalizes the common functional losses of these proteins in disease states.

Oxidative Stress Markers in Aging and Disease. Data analysis of proteomic changes in an aging heart were completed. We also demonstrated the feasibility of using nitro-, chloro-, and bromotyrosine as staged stress markers in the lung upon exposure to cigarette smoke and other toxicants presented at the 2008 National Meeting of the Society of Toxicology. We established proteomic sample work-up protocols that minimize reduction of nitrotyrosine to aminotyrosine. Recently, we detected in mouse heart and human plasma a new class of protein-oxidative products (i.e., hydroxylated tyrosine, also known as dihydroxyphenylalanine [DOPA]) and its related one-electron oxidation product, DOPA-quinone. This discovery is made possible by the high mass accuracy instrumentation available at EMSL that can detect differences in 1 amu, thus differentiating DOPA (+16 amu) from DOPA quinine (+15 amu) from aminotyrosine (+14 amu). Protein-bound DOPAs are substantially more abundant than nitrotyrosine and have been associated with the elicitation of cellular antioxidant defense pathways and thus represent an important measure of stress response. Moreover, the detection of DOPA in plasma samples indicates that our proteomic methods have sufficient sensitivity to provide disease biomarkers. Work with EMSL and other collaborators resulted in the identification of stress pathways in neurodegeneration; an associated manuscript on this topic is published in the *Journal of Proteome Research*.

Tools for Single Molecule Detection in Living Cells. Understanding the consequences of oxidative stress in the living cell requires highly sensitive probes for monitoring the fate (degradation, cell localization, aggregation) of oxidation-sensitive proteins; therefore, new classes of cell-permeable single molecule fluorescent probes are being synthesized that can be bound to complementary peptide sequences expressed on proteins of interest. Using anisotropy measurements sensitive to hydrodynamic radii, we have defined cell conditions that prevent probe aggregation during labeling. Moreover, we have defined a suite of tag-probe pairs for future testing in cell models, which is critical to the next step of describing cellular responses to stress.

Systems Analysis of the Dynamics of Membrane Architecture, Composition, and Function—Proteomic, Metabolomic, and Metallomic Characterization

Jon M. Jacobs, Thomas O. Metz, James A. Campbell, David G. Camp II,
David W. Koppenaal, Richard D. Smith

◆ This project is developing advanced techniques for quantitative protein analysis of and approaches to characterize both the metabolite and metallomic component of *Cyanothece* 51142. The study of such single-celled nitrogen (N_2) fixing and photosynthetic organisms can provide important insights into the molecular pathways used to perform these complex but energetically important reactions. ◆

This project will develop and apply new approaches for quantitative proteomic measurements to establish and use nontargeted procedures for characterization of the metabolome and to perform global metallomic analyses of the photosynthetic organism *Cyanothece* 51142. We will exploit advanced mass spectrometric methods previously developed at PNNL for global proteomics measurements and apply these in a global systems biology study of *Cyanothece*. This organism is unique in that it has developed a type of temporal regulation in which N_2 fixation and photosynthesis occur at different times throughout a diurnal cycle, including very high levels of CO_2 fixation and storage during light cycles for use in dark cycles. We will develop approaches using pulse chase stable isotope labeling to measure protein turnover rates and dynamics quantitatively, methods and procedures to obtain broad coverage of the metabolome, and procedures and techniques for global metallomic characterization.

During FY 2008, we furthered work in all three main focus areas. We utilized the previously created robust mass and time tag database for the *Cyanothece* 51142 organism to perform quantitative measurements based on liquid chromatography-Fourier transform ion cyclotron resonance (LC-FTICR) to characterize protein turnover events throughout the diurnal cycle. The quantitative analysis of multiple sets of *Cyanothece* samples from the Pakrasi Laboratory specially grown in a time course-based manner throughout a diurnal cycle. We have identified over 40,000 unique peptides from over 3400 proteins representing ~64% of the currently annotated genome. Additionally, 506 of 1989 annotated hypothetical proteins (25%) were reannotated as unknown due to the detection of multiple peptide sequences. This proteomic-assisted genome analysis has been accepted for publication in *Proceedings of the National Academy of Sciences*.

We have taken all previously quantitative analyses performed in FYs 2006 and 2007 and are in correlating results with complementary microarray experiments. Additional analyses performed in FY 2008 included refining and completing a metabolic labeling experiment to distinguish newly synthesized proteins within a certain timeframe and potentially to assign a synthesis rate for each protein.

With regard to metabolomic studies, additional targeted MS/MS studies conducted did not provide sufficient information for the structural characterization of those metabolite features displaying interesting behavior in metabolomics analyses of *Cyanothece* 51142 time-course samples. Despite initial expectations, it is unlikely that high-resolution LC-MS data alone can provide sufficient information for *de novo* metabolite identifications. By contrast, corresponding LC-MS-based lipidomic analyses of *Cyanothece* time-course samples revealed four main classes of lipids: monogalatctosyldiacylglycerol (MGDG), digalactosyldiacylglycerol (DGDG), sulfoquinovo-syldiacylglycerol (SQDG), and phosphatidylglycerol (PG) that have been reported in Synechocystis 6803. Analysis of the time-course data revealed similar interesting behavior among the lipid species (i.e., a cycling abundance pattern in response to incubation in the dark or light). In particular, a species with m/z 770.5802 with exemplary cycling abundance was tentatively identified as 16:0, 18:2-MGDG. Final data analysis will likely reveal other molecular species of MGDG, DGDG, SQDG, or PG perturbed during the diurnal growth cycle.

For metallomic studies, the objectives are to determine metal cycling behavior in whole cells and correlate the results with the proteomic/metabolomic studies. Whole cell samples were collected every 4 hours during dark and light cycles, prepared and analyzed by inductively coupled plasma/optical emission spectroscopy (ICP/OES) analysis, and further diluted for ICP/mass spectrometry (MS) analysis. Calibration curves for each metal were obtained for quantitation. We were limited because the amount available for the sample duplicate was approximately 1 mg; any difference in water content would potentially impact results. Overall, ICP/OES and ICP/MS show promise for analysis of whole cells, and similar trends were observed for both techniques. However, replicate samples need to be analyzed to determine reproducibility. Minor trends were observed, but results were not as definitive due to concentrations based on cell dry weight.

New samples have been recently obtained that were taken every 2 hours over a 48-hour cultivation period. Cell samples were rinsed three times with ultra pure doubly-distilled water prior to shipment; no additional washing will be performed before analyses. The samples are being examined using ICP/OES and ICP/MS for a range of metals to determine cycling behavior. Results will be based on metal concentration/μg chlorophyll.

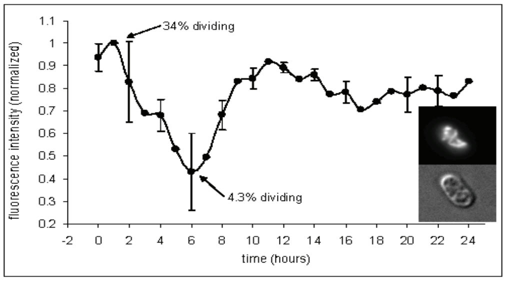
The Dynamic Changes in the Molecular Interactions Along the Circadian Rhythm

Galya Orr, David J. Panther

◆ Cyanobacteria undergo a complex circadian rhythm that must originate in part from dynamic changes in protein expressions and in the assembly and disassembly of protein complexes and cellular structures along the cycle. The goal of this project was to develop and apply fluorescence techniques to identify and characterize dynamic changes in protein expression and interactions and the formation of protein complexes along the circadian rhythm in *Cyanothece* 51142. By focusing on the CmpABC bicarbonate transporter, a protein complex assembled in the cytoplasmic membrane, we gained a new understanding of the mechanisms underlying the generation of the rhythm in the CO_2 uptake and concentrating system. ◆

The aim of this research was to elucidate mechanisms that underlie the unique ability of certain cyano-bacteria to go through a complex circadian rhythm while executing two antagonistic pathways: photosynthesis and nitrogen fixation. Because this ability must originate at least in part from the previously mentioned dynamic changes in molecular interactions and formations of protein complexes along the cycle, we developed and applied fluorescence techniques to investigate these changes in the intact cyanobacterial cell. The techniques, which rely on immuno-fluorescence tagging, include fluorescence resonance energy transfer (FRET), among other approaches. The application of immuno-fluorescence techniques in the intact bacterial cell has been limited, especially in cyanobacteria that have their own pigments and associated auto-fluorescence. The establishment of these powerful techniques in prokaryotic cells could aid significantly in their investigation.

Our research focused on the high-affinity CmpABC bicarbonate transporter, which plays an important role in the cyanobacterial CO_2 concentrating mechanism. Carbon uptake is minimal in the dark and is significantly increased in the light when photosynthesis and carbon fixation take place, but the underlying mechanism is still unclear. By developing quantitative fluorescence techniques and reagents specific to *Cyanothece* 5112, we were able to investigate dynamic changes in the expression patterns of the CmpABC transporter's subunits and their assembly in the cytoplasmic membrane along the circadian rhythm.



DNA content was quantified using a specific fluorescent probe (inset), showing a significant decrease during the light period. The decrease indicates the occurrence of cell division between L2 and L6. The decrease in DNA content was blocked by a drug that inhibits photosynthesis, unraveling the direct relationships between the two cellular processes.

During this project, we established immuno-fluorescence methods and multi-channel imaging for investigating periplasmic proteins in the intact *Cyanothec*. Using the antibody against the CmpA subunit of the transporter, we established the method for introducing antibodies into the periplasm and the isolation of two different fluorophores for multicolor fluorescence imaging in cyanobacteria. The new methods enabled the simultaneous investigation of multiple proteins and the detection of protein complex formation and molecular interaction dynamics using FRET.

Using the established methods, we have been quantifying the expression and insertion of the subunit in the cytoplasmic membrane. By tagging each antibody with 1 to 2 dye molecules, it has been possible to estimate the number of subunits within a fluorescent spot using single-molecule fluorescence techniques. Taken at distinct times along the circadian rhythm, this information has allowed us to determine changes in the cytoplasmic membrane expression of the protein along the cycle. Using the immuno-fluorescence method, we also detected a circadian rhythm in the CmpA subunit membrane insertion by flowcytometry. Our study is the first to show the cyclic pattern of the protein expression and insertion into the cytoplasmic membrane of the intact cell.

To study the assembly of CmpA and CmpB subunits in the cytoplasmic membrane, we developed the antibody against the periplasmic domain of CmpB. Together with the antibody against the periplasmic domain of CmpA, a new antibody has enabled the detection and quantification of fluorescence co-localization between the two subunits. Using fluorescent probes, we quantified changes in DNA content along the circadian rhythm, and with specific inhibitors of photosynthesis and respiration, we identified cell division pattern along the cycle and underlying mechanisms. Because cyanobacteria are capable of transforming solar into chemical energy (photosynthesis), they play an influential role in the evolution of the terrestrial environment and are largely responsible for today's oxygen-rich atmospheric environment.

This project has developed new ways to identify molecular interactions in living bacterium, cell division patterns, and underlying mechanisms to enable a better understanding of how light energy is transformed by the bacterium for its needs during the rhythmic cycles in carbon and nitrogen fixation.

The Tree-of-Life Chip for Examination of Ecosystem Structure and Function

Jon K. Magnuson, Scott E. Baker, Ruimin Tan, David E. Culley, Jason E. McDermott, James R. Collett

◆ The Tree-of-Life (ToL) chip is an advanced nucleic acid detection tool for assessing the diversity and key physiological functions of a wide variety of eukaryotic microorganisms within a complex ecosystem. This will be of tremendous value both in discovering early warning indicators of physical or chemical perturbations in an ecosystem and in rapidly assessing the presence or absence of these biomarkers, thus facilitating timely responses to environmental insults to freshwater or terrestrial ecosystems. ◆

High-density nucleic acid microarrays (chips) that contain thousands of oligonucleotide probes (spots) have been used for simultaneously examining all genes in an organism's genome and more recently for assessing a variety of prokaryotic microorganisms (bacteria and archaea) in complex environmental samples. However, microarray technology has not been used to investigate simultaneously multiple taxa of eukaryotic microorganisms and their functions in complex ecosystems. The objective of this project is to develop a general eukaryotic microbe Tree-of-Life (ToL) chip for assessing taxonomic and functional diversity in a wide variety of soil or aquatic ecosystems as a method for identifying biomarkers indicative of stress to those ecosystems.

For the taxonomic microarray, we developed a set of probes for the widely used ribosomal ribonucleic acid (rRNA) genes in order to detect and classify the eukaryotic microbes present in a sample. Another technological gap we seek to address is the design and use of microarrays for the assessment of a variety of physiological functions within an ecosystem. Through development of a chip that assesses key physiological functions, we may discover sensitive early warning indicators of ecosystem stress that precede changes in the population of a particular organism and thus give time to prevent more extensive damage to the ecosystem. We are focusing on the hyporheic zone of freshwater rivers, the water-saturated sediment zone where groundwater and river water meet. This boundary in a river ecosystem is of interest and concern because it is the first site of interaction of potentially contaminated groundwater with surface waters.

The principal challenge in building the ToL chip is retrieving, aligning, and analyzing thousands of gene sequences from public databases to develop the oligonucleotide probes. To assess the eukaryotic taxa present, we are using the ITS1/5.8S/ITS2 region of rRNA genes. The relatively high conservation of these rRNA sequences through evolutionary time makes them the preferred target for the molecular classification of organisms. The sequences used represent a broad taxonomic spectrum of fungi, green algae, and diatoms. This task was completed in FY 2007 for the phylogenetic chip, but the development of the physiological function chip was estimated to exceed the time and resources available in the project. Therefore, it was tabled in order to focus on development of the phylogenetic (ToL) chip, tools to analyze, and the analysis of the 48 samples from the periphyton uranium exposure experiment.

Early in FY 2008, the ITS rRNA sequences for ~1600 species of fungi, 300 diatoms, and 300 green algae were used to complete the design of the probe set for the ToL chip (microarray). For each of these three groups, a tiling array approach was taken to develop a set of oligonucleotide probes that were 25 nucleotides in length (25mers). Many of these 25mer probes matched multiple species, so a single copy of each of these was retained. In addition, one to five unique 25mer probes were retained for each species. The end result was a set of ~60,000 probes that corresponded to unique species or higher taxa such as genera, families, and phyla. The probe set was provided to Affymetrix® and printed in triplicate to form the 180,000-feature ToL chip.

During most of FY 2008, the project focus was on developing deoxyribonucleic acid (DNA) extraction and polymerase chain reaction amplification protocols for various dirty samples (soils and periphyton) and subsequent analysis of the amplicons by the ToL chip. These extraction and PCR techniques were used to amplify the ITS rRNA region from mixed microbial community DNA samples. The amplicons were labeled and hybridized to the ToL chip. Initial environmental microbial community samples selected for analysis included a shrub-steppe soil, an orchard soil, a native Columbia River periphyton sample, and simple cases of pure fungal cultures. Replicate analyses were performed on these samples that allowed us to prove that the chip could discern differences between communities and that those differences were reproducible (i.e., the replicates gave the same patterns). Data from these samples were also used to develop tools and techniques necessary to sort the ToL chip data and determine the valuable conclusions.

Finally, 48 samples from a ^{238}U-exposed periphyton experiment were analyzed using the microarray. Particular groups of fungi and green algae that may be affected by the uranium exposure were identified using the ToL chip and associated statistical analysis tools. These organisms would be candidates for developing and assessing biomarkers indicative of environmental stress from uranium exposure.

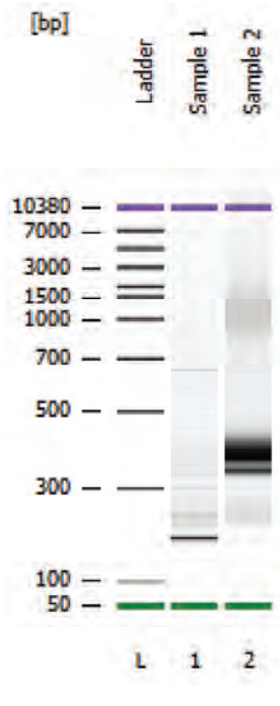
Using Subtractive Hybridization to Identify Biosignatures of Perturbed Microbial Communities

Vanessa L. Bailey, Bobbie-Jo M. Webb-Robertson

◆ The ability to assess the indigenous microbial communities perturbed with contaminants in the absence of pre-existing knowledge would significantly enhance efforts to predict the impact of contaminants and their ultimate fate at DOE legacy sites. In addition, such a capability would advance the understanding of key microbiological and geochemical processes that control the effectiveness of in situ immobilization as a means of long-term stewardship. ◆

Genes encode fragments of messenger ribonucleic acid (mRNA), whose population isolated from a soil represents the total genetic and metabolic potential of the soil biome. Within this diverse mixture, some mRNA species are associated with contaminant bioattenuation, while many will be involved in unrelated cellular processes. We have used subtractive hybridization-polymerase chain reaction (SH-PCR) strategies to separate these two populations and amplify the sequences unique to contaminant exposure. Briefly, SH-PCR strategies are used to compare two mRNA populations (contaminated and uncontaminated communities) to “filter out” mRNAs common to both samples and allow for collection of mRNA fragments uniquely expressed in one population relative to another. The use of SH-PCR-based techniques has not been reported for soils and is not globally in sediments. Recently, SH-PCR has been used to compare microbial communities inhabiting the rumen of cattle.

We hypothesize that SH-PCR can be successfully applied to undefined environmental microbial communities, and developing this method is the primary objective of this research project. We are also developing an SH-PCR procedure to study gene expression in soil/sediment microbial communities using chromium as a model contaminant. This task is approaching completion, and what remains is refining the adapter sequences to keep the subtracted library free from adapter artifacts that can “clutter” sequencing. In addition, we are using computational approaches to identify patterns of gene expression that meet our criteria for biomarkers of environmental perturbation. Another task is seeking biomarkers of uranium perturbation in periphyton communities.



Fragments uniquely expressed in Cr-exposed soil (Sample 1) and fragments no longer expressed following Cr exposure (Sample 2).

Finally, we plan to combine our approaches to seek biomarkers of uranium contamination in model hyporheic sediments exposed to uranium-contaminated groundwater.

During FY 2008, our efforts focused on conducting the subtractions and sequencing the subtracted libraries. Detected in mesocosm sediments, periphyton, and chromium-exposed soils, unique fragments have been found consistently in separate replicated subtractions. While this approach is not inclusive of all unique fragments, it offers a first glimpse inside the “black box” without preexisting sequence information. The procedures were conducted on total RNA, which would include unique fragments of ribosomal origin, thereby identifying unique species in the mesocosm and periphyton communities. Also, unique fragments could be from the mRNA pool, which would suggest unique functions. Because of the short time (2 hours) of chromium exposure, it is unlikely that the species composition would have shifted, so it is anticipated that these fragments are dominantly of gene origin. We also conducted “reciprocal” subtractions for all treatments in order to detect genes that are uniquely lost following exposures or treatments.

The soil chromium libraries sent for sequencing continue to include gene sequences consistent with the unculturable species *Rubrobacter xylanophilus*, which is known to grow in desert soils. Specifically, we detected its pseudo-uridine synthase gene robustly (i.e., different fragments of this gene were detected in each of two separate subtractions) and its penicillin amidase gene. We resolved past subtraction issues by modifying both our subtraction protocols and a commercially available kit for subtractive hybridization of bacteria to work in soils, sediments, and periphyton.

In FY 2008, we completed our analyses of the model systems (periphyton and mesocosm), and the sequences have been provided to the integration task. The soil chromium exposures have been completed, and the library is under analysis and being prepared for publication.

Chemistry

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

Clement R. Yonker, David J. Heldebrandt

◆ "Switchable Solvents" shows promise as attractive CO_2 capture and transfer agents. These non-corrosive carbon dioxide binding organic liquid (CO_2BOL) systems offer tremendous engineering advantages compared to standard ethanolamine (MEA) corrosive liquid, solid, or multi-phase chemical trapping agents. CO_2BOLs are highly tunable, reversible, and recyclable. ◆

This research is to produce a readily reversible, selective CO_2 trapping and transportation solvent that contains an amidine or guanidine base and an alcohol. The ultimate economic and engineering feasibility of this project requires fundamental investigations to answer basic science issues before the system can optimally approach the DOE target of 10 tons of CO_2 per day. We envision the project scope and research plan to generate the adequate knowledge required to optimize the process at the molecular level prior to engineering and optimization on the pilot or industrial scale.

The current regenerable post-combustion CO_2 capture and removal systems are energy inefficient and uneconomical, also making them impractical. This research will develop a reversible liquid-based CO_2 trapping and transport agent that is more energy efficient and durable than conventional post-combustion CO_2 trapping agents. The MEA process will be used as the benchmark for this development. The CO_2BOL system will bind CO_2 under flue gas conditions, transport bound CO_2 in the liquid phase, and release the CO_2 under ambient or mild conditions for repeated use. Results achieved from this work will bolster green technology with the development of a readily reversible, environmentally responsible, recyclable CO_2 trapping and transport agent.

In FY 2008, CO_2BOLs were investigated for their physical and chemical properties during CO_2 uptake. CO_2BOLs 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 appeared 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 post- and pre-combustion CO_2 capture. CO_2BOLs chemically bind CO_2 weakly as alkylcarbonate salts that require lower temperatures of CO_2 release compared with bicarbonate salts observed in aqueous MEA systems. CO_2BOLs's organic composition and lower specific heat require far less energy for stripping CO_2 than conventional aqueous/MEA systems, which are constrained by the high specific heat of water as well as the large volumes of water needed to maintain their liquidity. It was determined that CO_2BOLs can be formed competitively in the presence of water by dilution in a large excess of alcohol. If water is in significant quantities, undesirable bicarbonate salts will be formed; however, they can be reduced more efficiently than MEA systems due to CO_2BOLs's lower heat requirement. Alcohol was shown to have a limited role in the thermodynamics of CO_2 binding, while the base showed some influence on both ΔH and ΔG. The low energetics of CO_2 binding and release is likely due to the weak ion pairs of the CO_2BOLs and independent of the pKa of the base. With multiple alcohols and bases and their potential chemical modification, CO_2BOLs can be tuned at the molecular level to enhance their physical and chemical properties.

In FY 2009, research will chemically fine-tune CO_2BOL to meet CO_2 absorption kinetics engineering requirements, durability standards, and most importantly, cost. During this phase, CO_2BOL systems will be fully probed to provide a complete molecular understanding the CO_2 binding and release mechanism. Once this molecular understanding is complete, it will be used to manipulate CO_2BOLs to meet the engineering requirements needed to make the process feasible. A simulated process model will be created with Chemcad or Aspen+ to predict system feasibility and cost. After a simulated model is created, synthesis of the selected solvent system will be manipulated and scaled up to meet system demands and cost.

In FY 2010, the project will continue to optimize the selected system in tandem with process engineers, producing a working bench-scale model by the end of the third year. The recyclability of the CO_2 trapping system will be studied and optimized with batch and continuous flow methods. Lifetime and durability of the CO_2BOLs will be investigated and optimized. A laboratory-scale demonstration system of the continuous-flow CO_2 trapping and removal will show the efficiency, recyclability, and cost elements of the system. A 10,000-ton goal should be within the project scope.

Advanced Gas Separations Based on Highly Efficient Microchannel Component Technology

James C. Hayes, Richard M. Williams, Paul H. Humble, Randy R. Kirkham

◆ The objective of this project is to perform focused experimental and theoretical research aimed at demonstrating room temperature pre-concentrators and gas separation devices for the collection and/or purification of relevant atmospheric constituents, with particular focus on nuclear proliferation signatures. If successful, this would lead to a new generation of smaller, lower power, more efficient air sampling instruments that can meet the challenging criteria established by the national security user community. ◆

Nearly all signatures that indicate a national security threat are dilute and typically require significant preprocessing to put the sample into a measurable form. The gas separations technology used in air sampling instrumentations for nuclear explosion monitoring programs is generally based on cryogenically cooled bulk separation columns packed with absorbent materials. While these techniques are robust and time proven, they suffer in that they are bulky, less efficient, and require cryogenic cooling, all of which add to the overall system footprint. PNNL is a leader in the design and fabrication of advanced microchannel technology used for a wide array of applications (heat exchangers, gas/liquid separations, and fuel cells). This project is aimed at improving high-volume gas purification and low-volume gas separations for nuclear explosion monitoring instrumentation and other national security needs by incorporating novel microchannel technology.

During FY 2007, a novel approach was studied regarding the replacement of bulk adsorption columns with micro channel technology. The key to improving the efficiency of preconcentration devices using microchannel technology lies in their small lateral dimensions (under 1 mm) and short flow paths. By reducing the size of the channel cross-section to submillimeter scales, Laminar flow is achieved, and the efficiency of heat and mass transfer are greatly increased. Further, the pressure drop across a microchannel device can be considerably lower than that found in most packed columns, which in turn reduces the electrical demands on the compressor moving air through the system.

In addition to microchannel technology, other novel approaches aimed at concentrating trace species out of ambient air were considered. Principal among these was a unique adaptation of a common industrial gas processing scheme known as pressure swing adsorption (PSA). This technique does not require heating or cooling to collect atmospheric constituents; rather, it utilizes changes in pressure to achieve the uptake of specific gases. If this PSA technique can be optimized for the collection of relevant atmospheric species, then a simple, low-power gas processing scheme can be designed to meet our objectives.

During the project's first year, primary focus was placed on testing a microchannel xenon preconcentrator. Xenon is an important chemical from a proliferation perspective, as detection of trace quantities of radioactive xenon can be linked to nuclear events. Research was conducted to determine a suitable adsorbent material for xenon that could be deposited on the inner surfaces of a microchannel device. After several key experiments, single-walled carbon nanotubes were chosen, and a spray technique was developed for coating the surfaces. Simultaneously, a computer simulation of the adsorption process in the microchannel was developed.

Findings from both numerical simulation and experimental results suggested that more adsorbent material was needed than could be coated onto the inner surfaces of these microchannel devices. An alternative preconcentrator design adopted at the beginning of FY 2008 is a hybrid device combining microchannel elements into a conventional packed column. A commercial tube-in-shell heat exchanger was modified in such a way that activated charcoal (adsorbent material suitable for xenon) could be packed in and around the large number of small-diameter inner heat exchange tubes. The inner tubes were connected to a temperature-controlled water source for heating and cooling, while the remainder of the device containing the activated charcoal was connected to inlet air stream (at high pressure). During operation, the device is cooled to 5°C while high-pressure air flows through the charcoal, collecting xenon from the air. After several minutes, air flow is stopped and the pressure reduced while water flow is switched to hot (95°C). A vacuum pump is then used to "pull" remaining gaseous species from the heated trap and transfer them to a temporary collection container for further analysis. Results showed that a substantial amount of xenon was collected from ambient air using this technique.

The final phase of this research involved the development of a system that uses two traps in a parallel sequential configuration. In this way, one trap is collecting xenon while the other is releasing it. The adsorption/desorption modes of the traps are then switched so that collection is continuous rather than batch mode. This research phase resulted in a complete design concept for a non-cryogenic xenon collection system, meeting the principle objectives of the project.

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 for terrorists to use biological agents is a real threat. The goal of this project is to develop a low-cost, portable device for the rapid detection of biothreats that can 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 will develop superparamagnetic nanomaterials functionalized with bioagent capture probes; use those materials in novel microfluidic devices for simultaneous capture, preconcentration, purification, and separation of multiple bioagents; and integrate optical detection with the microfluidic device to allow for the rapid measurement of multiple biothreats in liquid samples or extracts. The overall objective of this research is to demonstrate a rapid (under 20 minutes), multiplexed (more than 3 bioagents) assay using a simple, low-cost, integrated microfluidic/optical detection platform.

A multidisciplinary team of scientists and engineers at PNNL have made significant progress toward our goals, having demonstrated separation and detection of two different fluorescently-labeled magnetic nanoparticles in a microfluidic device. Key accomplishments during this first year of the project include the following:

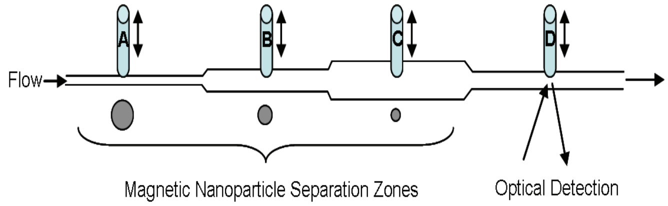
- Twelve different superparamagnetic nanoparticles were evaluated for assay suitability, including fluidic behavior (flow-path wall adsorption and the ability both to functionalize with antibodies and to separate nanoparticle mixtures).
- The nanoparticle capture efficiency was evaluated under different flow conditions and flow path geometries in order to guide microfluidic device fabrication specifications.
- A model sandwich immunoassay based on botulinum neurotoxin Type A heavy-chain fragment (BoNT/A-HC) detection was chosen.
- An early microfluidic device design was fabricated and tested.
- An automated mechanism for applying and removing high-strength magnetic fields was designed and fabricated.
- A novel, compact, high-power light source was identified for integration with the microfluidic device.

The twelve nanoparticles were downselected for further work and have features that will lead to rapid/sensitive assays, including the ability to capture with high efficiency, high antibody loading, and favorable fluidic behavior.

An initial microfluidic device was designed and tested using the model assay. Using fiber-optic guided laser-induced fluorescence, assay detection limits were shown to be in the hundreds of picomolar range (tens of micrograms per liter) for BoNT/A-HC without any optimization of the fluidic device or optical detection approach. Significant improvements in the limits of detection are expected.

Video of nanoparticle capture and release was used to improve understanding of the process and revealed interesting nanoparticle behavior (i.e., nanoparticle release results in uniform and complete dissolution/deaggregation thought to be the result of rapid repulsion of NPs that were tightly captured together in a microfluidic channel). The potential to exploit this unique behavior will be investigated in future research.

The automated magnet positioning manifold is ready for integration and testing with microfluidics and will be used to trap and release nanoparticles selectively at four locations along the length of a microfluidic flow path. A small multi-wavelength light source based on LED-coupled luminescent light pipes will also be integrated with the microfluidic chip. These improvements will allow significant progress toward a fully integrated device for sensitive and rapid multiplexed biodetection.



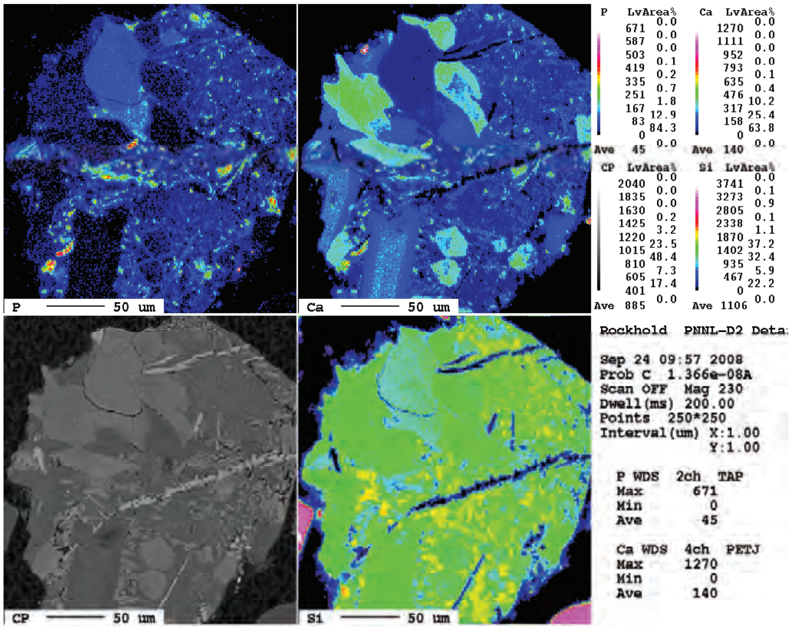
Four-stage microfluidic chip with 4 independently controllable magnets for magnetic nanoparticle separation, sequential release and detection.

Biogeochemical Perturbation Methods for Immobilization of Deep Vadose Zone Contamination Using Reactive Gases

Mark L. Rockhold, Tim J. Johnson, Jim E. Szecsody, James P. McKinley, Thomas A. Blake,
Tom W. Wietsma, Matt A. Covert, Martinus Oostrom

◆ This study evaluates the feasibility of using reactive gases for remediation of metal and radionuclide contamination in deep unsaturated sediments at Hanford. The use of gas-phase remediation technologies potentially provides a means for subsurface remediation that poses little to no risk of exposure to workers and minimal to no risk for the mobilization of contaminants that would occur using other remediation methods that rely on the addition of reagents to the aqueous phase. This research could potentially lead to low-risk, cost-effective methods for remediation of subsurface contamination at DOE sites such as Hanford. ◆

Remediation of radionuclide and metal contamination in the deep vadose zone is a particularly challenging problem because: 1) conventional treatment approaches involving aqueous injection of reactive chemicals pose an increased risk for mobilizing contaminants and displacing them deeper into the vadose zone or underlying aquifer systems, and 2) the vadose zone is aerobic, so remediation methods that rely on the creation of reducing conditions tend to be temporary, owing to rapid re-oxidation by gas-phase oxygen diffusion following treatment. Unlike aqueous injection of reactive chemicals, the gaseous injection strategy proposed for this research poses little to no risk for mobilizing vadose zone contamination. Our strategy relies on the temporary creation of reducing conditions in combination with phosphate mineral formation for contaminant sequestration, so re-oxidation should not be a significant issue. This research will evaluate the use of novel gaseous phosphorus compounds and new treatment strategies applicable to the remediation of numerous metals and radionuclides.



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          0.0              0.0
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          0.1              0.0
    419                 793
          0.2              0.1
    335                 635
          0.7              0.4
    251                 476
          1.8             10.2
    167                 317
         12.9             25.4
     83                 158
         84.3             63.8
      0                   0
          0.0              0.0
Ave  45          Ave  140
 CP LvArea%      Si  LvArea%
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   2040                3741
          0.0              0.1
   1835                3273
          0.0              0.9
   1630                2805
          0.2              0.1
   1425                2338
          3.2              1.1
   1220                1870
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   1015                1402
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    605                 467
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Ave 885          Ave 1106

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Thin section of a DMMP-reacted soil grain (basalt fragment) showing the relative abundances of P, Ca, Si, and a composite backscattered e-image from a JEOL JXA-8200 electron microprobe.

An experimental study was undertaken to evaluate the feasibility of using organophosphate compounds that can be transported in the gas phase as a source of phosphorus for mineral formation (e.g., apatite) and contaminant sequestration in deep unsaturated zones. Previous work with gaseous phosphate compounds used triethyl phosphate (TEP) for bioremediation. In the current study, we used both TEP and another chemically similar compound, dimethyl methylphosphonate (DMMP), which has a higher saturation vapor pressure (128 v. 52 Pa, 25°C). Batch degradation and gas transport experiments were performed to quantify rates of conversion of the organophosphate compounds to inorganic form and the transport of these compounds in unsaturated Hanford sediments.

Batch abiotic degradation experiments in aqueous solutions with and without sediment (in both oxic and reducing conditions) indicate that both TEP and DMMP are relatively recalcitrant. Slow conversion from organic- to inorganic-P forms occurred (less than 5% in 3 months) under high temperature (80°C) and highly alkaline pH conditions. TEP and DMMP biodegradation to PO_4 was minimal over a similar time period using concentrated solutions of in situ microbes (10^9 CFU/mL) with no other growth substrates present. Gas transport studies with FTIR monitoring spectroscopy show that these compounds also adsorb strongly to unsaturated sediments from the Hanford Site to the extent that no breakthrough was observed even after more than 1000 pore volumes of gas exchange and the complete dessication of sediments. Methanol production was observed during the DMMP gas transport experiments, indicating that the lack of observed breakthrough of the original organophosphate compounds was attributable to both adsorption and reaction processes. FTIR reflection spectroscopy and microprobe analyses were performed to identify and quantify adsorbed species and possible secondary Ca-P mineral formation. Although there is some evidence for secondary Ca-P mineral formation, the strong sorption characteristics of these compounds suggest that their usefulness for the intended purpose may be limited.

Carbon Nanotube Materials for Preconcentration

Jay W. Grate, Richard Zheng, Leonard S. Fifield, Norman C. Anheier, 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 homeland security. The detection of explosives is critical to security applications ranging from defense and homeland security 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 the requirements for greatly enhanced chemical sensitivity and lower detection limits.

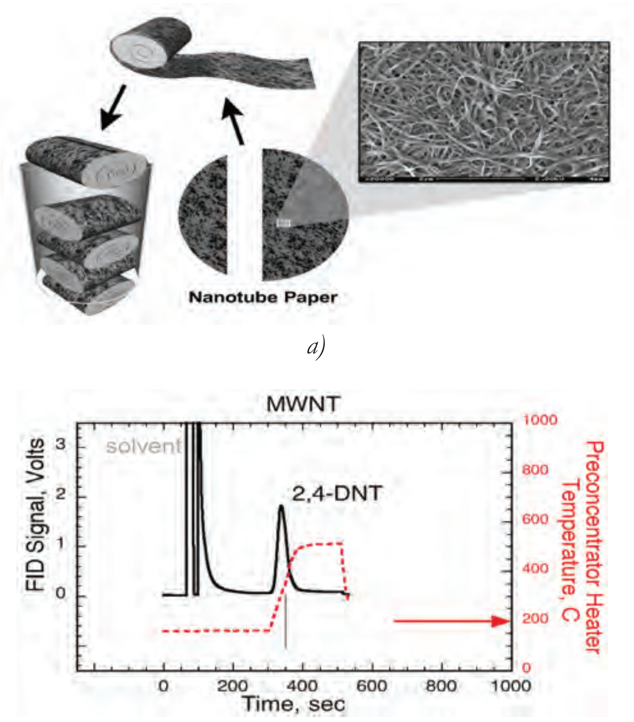
Under this project, we are investigating carbon nanotubes as a new material for use in thermally desorbed adsorptive preconcentrating devices. Carbon nanotube-based structures and devices could be used as collectors in monitoring applications and in trace detection instrumentation. In the latter case, the use of a preconcentrator could reduce detection limits, improve selectivity, and/or allow other instrumentation to be used as the detector.

In general, carbon nanotubes have many desirable properties for the preconcentration of vapors in analytical applications, including high thermal stability, extremely high thermal conductivity along the tube axis, electrical conductivity from semi-conducting to metallic, unique chemical interactions due to nanometer-scale C-C bonded molecular structure, unique architecture compared to most solid adsorbents, which are generally granular solids, amenable to synthetic modification, and their use can be scaled from nanometer to micrometer to macro-size applications. We anticipate a number of advantages and applications for carbon nanotube-based sorptive devices in chemical and explosives detection.

Our approach includes several elements. First, we investigated a wide range of carbon nanotube materials for their thermal stability, including systematic investigations from single-walled nanotubes (SWNT) to multiwalled nanotubes (MWNT) and comparisons with carbon fiber materials. We determined thermal decomposition temperatures for several of these materials. Second, we are examining various physical forms (e.g., nanotube/bucky paper; Figure a) and geometries of nanotube materials for use in preconcentration and device applications. Nanotube paper converts a powdered material into a macroscopic form that can be used in flow-through applications. We are also developing packed beds of carbon nanotubes with satisfactory flow-through characteristics. Third, we are investigating synthetic modifications of nanotube materials. We have carefully selected chemistry for altering the surface properties in ways that are anticipated to alter the adsorptive characteristics and selectivity. Fourth, we have begun investigations into the thermal desorption of explosives molecules from the surfaces of carbon nanotube materials. These studies have used thermal gravimetric analysis to determine mass loss and vapor detection to observe the desorbed species.

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 illustrates the thermal desorption of 2,4-DNT from a MWNT sample as a packed bed. Desorption is observed with a peak at approximately 300°C.

In FY 2009, we will elucidate the desorption pathways for nitroaromatic explosives compounds from a variety of nanotube materials using programmed thermal desorption and gas phase analysis techniques.



a)

b)

a) Carbon nanotube paper showing an SEM image on the right and using nanotube paper to create a packed column on the left, b) thermal desorption of 2,4-dinitrotoluene from a packed bed of multiwalled carbon nanotubes on a programmed thermal ramp from 165 to 515°C at 4°C/second.

Catalytic Chemistry of the Weak Links in Lignins and Lignites

Z. Conrad Zhang

◆ This research is aimed at selective catalytic cleavage and quantitative determination of weak links in lignin and low-rank coals. The objective is to develop site-specific catalysts that can selectively cleave various oxygen linkages common in lignin and lignite structures. The knowledge to be generated through this project will help guide catalyst selection and process conditions in coal liquefaction and direct conversion processes to value-added products. ◆

Lignin is present in high concentrations from processed biomass and is a large component of many coals. The macromolecular structures of lignins and coals have been extensively studied, mostly based on analysis subsequent to pyrolysis. Because severe conditions were applied prior to the analysis (mostly by nuclear magnetic resonance), multiple chemical transformations occurred during pyrolysis are expected to make structural information less reliable. Lignin breakdown in a strongly basic aqueous alkali solution at low temperature has been in common practice in the wood pulping industry. For example, black liquor contains severely fragmented lignin components.

This project is focused on investigating organic base catalysts and ionic liquids as potential solvents for lignin. Lignin and lignites are known to be aromatic in their bulk structure, and catalysts such as alkali phenoxide and sodium benzoate as well as related aromatic polybases are expected to have a strong affinity in lignin and lignite structure because of this aromaticity. The project proposes to investigate these catalysts as a function of process conditions to determine if cleavage at selected oxygen linkages can be controlled under mild conditions without affecting the structural integrity of the lignin.

Hardwood lignin is insoluble in boiling water. Autoclave experiments with 0.005 M NaOH in water showed limited solubilization of the hardwood lignin at 100°C over 4 hours. On the other hand, guanidine carbonate added at 1% (pH 9.6) showed significant depolymerization of the lignin as evidenced by gel chromatography studies. The addition of H_2O_2 to the guanidine carbonate-lignin mixture showed additional dissolution of the lignin. Similar effects were found with sodium phenoxide. Thus, bases with more organic and aromatic properties showed the ability to dissolve lignin, which also indicates cleavage of some C-O bonds. These results were further supported by SIMS as well as Electrospray Ionization Mass Spectroscopy studies. A number of possible fragments from the base-catalyzed bond cleavage were identified. In addition to the catalysis in base, it was also discovered that lignin is soluble in an ionic liquid, [EMIM]Cl. This opens the possibility of using the ionic liquid as a solvent to solubilize the lignin, and various catalysts can be added to the ionic liquid to carry out various possible catalytic transformations.

Work then proceeded to evaluating similar base-catalyzed cleavage with coal-based lignite. It was similarly found that lignite became partially water soluble after depolymerization in the presence of sodium phenoxide. NaOH also solubilizes lignite, but the organic bases appear to be superior; moreover, the addition of a hydrogen peroxide oxidant further converts the lignite to a soluble product. The results are summarized in the table.

	Water	**NaOH**	**Guanidium Carbonate**	**Sodium Phenoxide**
No H_2O_2	0%	<15%	28.4%	34.2%
2% H_2O_2	n/a	<20%	40.0%	47.0%

Additional work is required to identify the fragments generated from this catalytic chemistry. Finally, a class of ionic liquids was evaluated for dissolution of lignite. It was found that solubility was according to the following order: [EMIM]TFA > [EMIM]PF_6 > [EMIM]BF_4 > [EMIM]Cl. This sets the stage for novel chemistry to be applied to the solubilization and catalytic conversion of lignin.

Even though the methodology is similar to those used for the study of biological molecules such as peptides and proteins, there exists a major difference between proteins and lignin and lignites. Proteins are linear molecules; by contrast, lignin and lignites are three dimensionally structured aromatic networks with little structural information available. Therefore, it is challenging to build a working methodology and description framework for lignin and lignite structures. Based on tandem mass spectrometry experiments of known lignins and lignites, a database will be constructed for common structures and substructure fragments. The establishment of such database will be helpful but not essential for the initial study because many of the common features of lignins or lignites need to be explored experimentally. It is a progressive effort that will accelerate the research in the later stage.

Cationic Ionic Hydrogenations: Developing Concepts and New Catalytic Processes that Substitute Inexpensive Metals for Precious Metals

R. Morris Bullock

◆ Transition metal hydrides function in a variety of contexts in catalysis, delivering hydrogen to organic substrates in hydrogenations and other reactions carried out on a large scale in the chemical industry. Our research has developed catalysts that use abundant, inexpensive transition metals in place of expensive precious metal catalysts. ◆

Traditional homogeneous catalysts for ketone hydrogenation use precious metals such as ruthenium or rhodium. Removing the mechanistic requirement for an insertion reaction opens the possibility of alternative mechanisms, including inexpensive alternatives to precious metals such as molybdenum or tungsten. We have prepared tungsten complexes with an N-heterocyclic carbene ligand that exhibited activity in catalytic hydrogenations.

The cationic complex $CpW(CO)_2(IMes)^+B(C_6F_5)_4^-$ (IMes=1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) serves as a catalyst precursor for ketone hydrogenation. To understand the reactivity and performance under catalytic conditions, our efforts have focused on determining thermochemical properties of the metal hydride complex $CpW(CO)_2(IMes)H$ that has a pK_a of 31.9 in CH_3CN. This indicates that the N-heterocyclic carbene ligand is an exceptionally strong electron donor since this pK_a value is more than 5 units larger than that reported for the related phosphine complex $CpW(CO)_2(PMe_3)H$. This is the first report of the pK_a value for any metal hydride that has an N-heterocyclic carbene ligand.

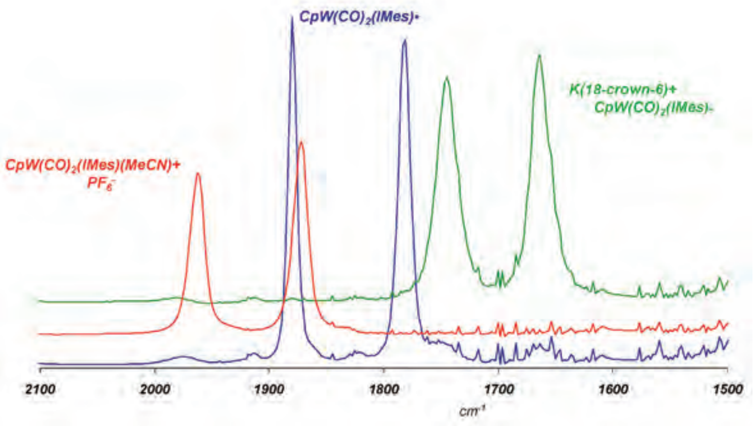
Although the metal hydride acidity is low, it can be deprotonated by KH in the presence of 18-crown-6, leading to the formation of $[CpW(CO)_2(IMes)]^-[K(18\text{-crown-}6)]^+$. This complex was characterized by IR and NMR spectroscopy and exhibits low energy bands for the CO ligands. The structure of this anion was determined by single crystal x-ray diffraction in collaboration with West Virginia University Professor Jeffrey Petersen. Electro-chemical studies of $CpW(CO)_2(IMes)^-$ show that it is easily oxidized with $E_{1/2}$=-1.60V (vs. Cp_2Fe^+/Cp_2Fe) in MeCN.

Hydride transfer from $CpM(CO)_2(IMes)H$ to $Ph_3C^+PF_6^-$ in MeCN generates the cationic complex $[CpW(CO)_2(IMes)(NCMe)]^+$. As shown in the figure, reaction of $[CpW(CO)_2(IMes)(NCMe)]^+$ with $[CpW(CO)_2(IMes)]^-$ leads to one-electron reduction of the cation by the anion, with both being converted into the 17-electron metal-centered radical, $CpW(CO)_2(IMes)$ that can also be synthesized by chemical reduction of $[CpW(CO)_2(IMes)(NCMe)]^+$ by Cp_2Co. $CpW(CO)_2(IMes)$ is a rare example of an isolable metal-centered radical of a third-row metal. Calculations using density functional theory showed that the unpaired spin is largely (~80%) centered on the metal.

Having measured the pK_a of the metal hydride and the oxidation potential of the metal anion, a thermochemical cycle can be constructed that provides the homolytic bond dissociation energy of the tungsten hydride bond as 65 kcal/mol. This value is surprisingly low for a third-row metal hydride and is about 4 kcal/mol lower than that reported for the phosphine complex $CpW(CO)_2(PMe_3)H$. This thermochemical information will allow us to design catalysts more rationally in reactions that involve proton transfer and hydrogen atom transfer reactivity of metal hydrides.

Our studies have also begun to examine the influence of different counterions on the reactivity of metal cations. Of particular interest has been the anion $N(SO_2CF_3)_2^-$, which has not been investigated in detail in catalytic reactions. Low-temperature ^{19}F NMR data indicates that this anion bonds to $[CpW(CO)_2(IMes)]^+$ through the oxygen. This anion is useful since it is readily displaced by ketones or other ligands, including H_2. Comparison with $CpW(CO)_2(IMes)OSO_2CF_3$ show that the $N(SO_2CF_3)_2^-$ anion is more readily displaced from the tungsten compared with $OSO_2CF_3^-$.

Catalysis plays a central role in the production of fuels, chemicals, and energy economy. The basic research in the catalysis of hydrogen conversions conducted under this project has led to new designs of catalysts for hydrogenation of organic substrates. By furthering understanding of catalysis at the molecular level, this project supports DOE's goals to accelerate innovation and create transformational solutions for energy sciences.



Infrared spectra of the CO bands of the cation $CpW(CO)_2(IMes)(NCMe)^+$, the anion $CpW(CO)_2(IMes)^-$, and the tungsten-centered radical $CpW(CO)_2(IMes)$.

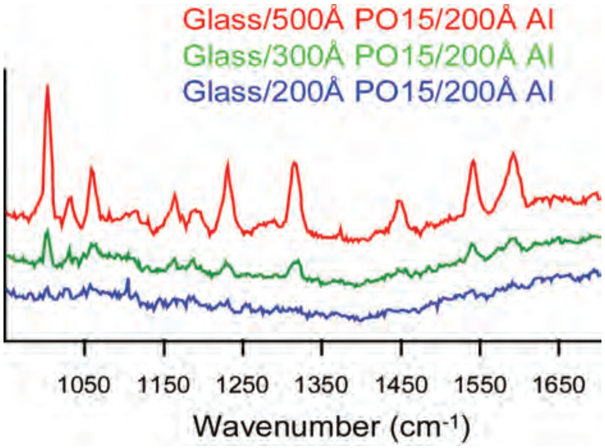
Characterization of the Local Order of Organic Thin Film Material by Combined Atomic Force Microscopy and Optical Microscopy

Dehong Hu, Asanga B. Padmaperuma, Xiuya Cai, Hong Qiao, Paul E. Burrows, Donald R. Baer

◆ This two-year project provided important structural and chemical information on organic thin films relevant to energy applications using a home-built microscope. The information obtained by the new microscope will benefit a broad range of research areas, including solid-state lighting and solar energy conversion. ◆

Organic thin film materials are involved in a broad range of emerging photonic technologies, including light-emitting devices and photovoltaics. Compared with conventional silicon-based semiconductors, organic thin film materials have the advantages of low cost, high efficiency, easy processing, and flexibility. Chemical information such as purity and molecular arrangement of thin films is critical for developing devices but difficult to characterize. In this project, we focused on two important properties. The first was the local order of thin films that was believed to affect the charge mobility of the film, but the overall effects of local order and disorder on the device performance were complex. The second focus was the chemical species of degraded film. Organic material degradation is a critical process related to the lifetime and efficiency of the device; however, as with developing devices, the degradation process and chemical structure-related information in the degraded material are difficult to characterize. An understanding of the degradation would guide the device manufacturing procedure to improve life time, efficiency, and stability.

The first aim of this project was to provide a new microscopy technique for studying the local order of organic thin-film materials. Developed in FY 2007, the technique enabled characterization of the local order of organic thin films in the nanometer scale. Because the local order of thin-film materials cannot be imaged on the nanometer scale by a conventional optical microscope at length scales below the diffraction limit, we designed and built a combined microscope based on a conductive atomic force microscope/scanning tunneling as well as an optical polarization microscope. Using this combined microscope, we studied the spectroscopic properties of organic thin films with resolution far beyond the optical diffraction limit. Such images were used to extract information on the extent of local nanoscale order in the thin film.



Raman spectra of PO15 organic films at different thicknesses.

In FY 2007, we demonstrated the capability of this microscope by introducing a metal tip on the top of organic layers and applying a voltage to the metal tip, where we observed photon emission. We tested alloy scanning tunneling and gold-coated atomic force microscope tips, both of which produced emission. The data supported our hypothesis of the ability to detect electroluminescence through local current injection. This is the first time electroluminescence from small organic molecules was observed through metal tips.

The second aim of the project was to study the degradation of organic thin film materials. Degradation occurs during device usage and the manufacturing process. In FY 2008, we used a home-built Raman microscope to study the degradation during device fabrication. The advantage of spectroscopy over the chemical method is that the latter involves disassembling the device, which may cause additional problematic reactions. Raman microscopy provided non-destructive high spatial resolution, chemical species identification, and depth penetration advantages.

The interface of an aluminum cap and organic films in the intact device was studied by Raman spectroscopy because it was suspected that the process of coating aluminum on organic thin film might degrade the organic material. We studied a series of films with different thicknesses as well as coating sequence and materials with our custom-built Raman spectrometer. The thickness-dependent Raman spectra revealed that the aluminum cap coating process causes damage on the surface to a depth of ~20 nm on organic films. On the other hand, the silver cap coating does not cause such damage under the same condition. We attributed the damage to the thermo-deposition of aluminum atoms, which reduced the organic material. To confirm the oxidation state change, we studied the organic film by x-ray photoelectron spectroscopy (XPS). We coated 5-Å thick layer of aluminum on the phosphine oxide compound PO15, and the XPS data confirmed that the phosphorus atom was reduced.

CO_2 Capture and Concentration Using Electrochemically Switchable Carriers

James J. Strohm, Aaron M. Appel

◆ The development of electrochemically switchable CO_2 carriers will result in a dramatic reduction in the cost of capturing CO_2 due to lower energy requirements, which is the result of higher efficiency of electrochemical compared with thermal processes. ◆

Electrochemically switchable CO_2 carriers have been previously studied, but they were either air-sensitive or unable to capture from dilute gas streams. This project will develop a new process for highly energy efficient capture and release of CO_2 based on electrochemically modulated complexation (EMC), which uses a CO_2 carrier solution that switches from the binding form to the release form through electrochemical reduction or oxidation.

In order to capture CO_2 from flue gas using EMC, a modified liquid spray adsorption process with improved carriers needs to be developed. New carriers will be developed that directly bind CO_2 in order to increase binding and release kinetics, decrease solvent restrictions, and improve system efficiency and design. Multiple carrier modifications will be quantified in order to help identify and design better CO_2 carriers for capturing CO_2 from flue-gas streams for overall process optimization and cost reduction. New CO_2 carriers will be synthesized and their structures, CO_2 loading, electro-chemical properties, CO_2 capture and release kinetics, ability to release CO_2 at elevated pressures, and tolerance to SO_x and NO_x, will be determined. Correlations between the structures, binding strengths, and electrochemical properties will be important for reducing process costs and improving system efficiencies by controlling the strength, selectivity, and reversibility of CO_2 binding. Improved carriers will allow for the development of an electrochemically switchable CO_2 capture process that will have a substantially lower energy requirement than the traditional monoethanolamine (MEA) process.

Two main areas of research will be focused on evaluating feasibility in a flow process and developing new CO_2 carriers. The first area will show that electro-chemically switchable CO_2 capture is worth pursuing for post-combustion CO_2 capture through an analysis of the energy requirements for the process and demonstration of the process in a flow reactor. The second area, carrier development, will allow for this process to move forward, as new carriers are required for post-combustion capture. In order to improve the carriers, basic research on new classes of carriers and their properties will be necessary in order to understand the requirements for developing optimized carriers. We are proceeding in both areas through ChemCAD modeling, process evaluation in a flow reactor, and through the synthesis of new possible carriers.

During FY 2008, three main tasks were performed: energy analysis, demonstration of a flow reactor, and initial carrier development. Electrochemically switchable CO_2 capture was evaluated using ChemCAD for a comparison of the energy requirements relative to the MEA process. The estimated energy requirements for sorbent regeneration were approximately one-third of that used in the MEA process, indicating that electrochemically switchable CO_2 capture is indeed capable of substantially improving the energy efficiency of post-combustion CO_2 capture.

The second task was demonstration of the electrochemically switchable CO_2 capture process in a laboratory-scale flow reactor using a previously studiedCO_2 carrier. Previous demonstrations have used batch reactors, but a flow process is generally preferred for a large-scale development. A flow reactor was constructed, and electrochemically switchable CO_2 capture was shown to work in a flow system, suggesting that development of this electrochemical process into an industrial scale flow process is feasible. Using the flow reactor, 10% CO_2 was concentrated to 97% CO_2, with 90% CO_2 capture from the feed gas stream.

The third task for FY 2008 was the initial development of new CO_2 carriers. Promising new direct-binding CO_2 carriers have been identified, and initial syntheses of the carrier precursors were successful. This first round of new carriers will help to determine the structural requirements for developing improved CO_2 carriers. The isolation and characterization of these new carriers is in progress and will continue into FY 2009.

The feasibility studies show that electro-chemically switchable CO_2 capture has significant promise, and therefore research in FY 2009 will primarily focus on the development of new carriers. New possible carriers will be studied in order to quantify CO_2 binding and release, therefore greatly improve subsequent carrier performance. In addition to carrier development, a second generation laboratory-scale flow reactor will also be developed in FY 2009 in order to better optimize the process. An improved lab-scale flow reactor will not only help demonstrate and study the overall process, but also be valuable for testing the next generation CO_2 carriers.

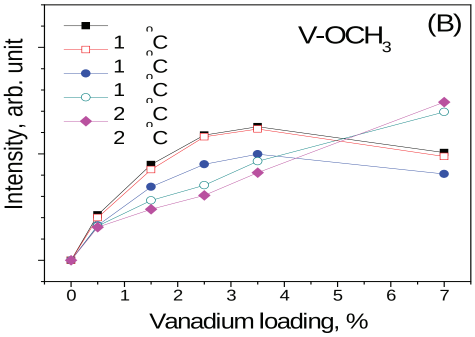
Combinatorial Operations Catalyst Research

Z. Conrad Zhang, David L. King, Guosheng Li, Dehong Hu

◆ The primary objective of this project is to create a new capability to enable combinatorial catalysis research under operando conditions. Such a system will allow for rapid and reliable research output supporting accelerated catalytic process development.◆

Combinatorial/high-throughput experimentation has been widely applied as a new tool to accelerate discoveries because a large number of experiments can be carried out simultaneously by using multiple reactors. Three general types of high-throughput experimentation systems screen catalysts according to their operational mode: 1) serial operation, using mass spectrometry, optical spectroscopy, or chromatography, 2) optical spectroscopy-based detection that is limited to reaction product analysis only, and 3) simultaneous product analysis and catalyst characterization limited to one catalyst at a time (applicable only to gas phase processes). So far, however, no system is available for combinatorial operando catalyst research. The objective of this project is to build and demonstrate a first-of-its-kind combinatorial operando system for accelerated catalyst research.

Under this project, we integrated Fourier transform infrared (FTIR) and Raman imaging techniques jointly to a combinatorial reactor assembly for real-time full product analysis and material characterization under operating conditions. Our high-throughput operando reactor consists of four parts: 1) FTIR spectrometry (the Vertex 70 can cover the full spectral range in experiments and can provide reliable spectral resolution at 0.5 cm^{-1}), 2) the multichannel reactor with Raman probe adaptors has six separated channels, each with a probe adaptor window for Raman measurement, 3) the infraredimaging system includes a focal plane array infrared detector, lens assemblies, and gold-coated mirrors, and 4) the Raman probes use commercially available optics fiber and standard optics parts, offering Raman spectroscopy as a reliable operando measurement for catalyst characterization.



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

Current studies at PNNL have focused on a Co/ZnO catalyst, which provides high selectivity to hydrogen at moderate ethanol conversions but has a decreased H_2 and increased CH_4 (methane) selectivity as conversion increases. It is believed that a combination of Co^0 and Co^{2+} is required for proper catalyst operation, but changes to this ratio (e.g., excess Co^0) may result in excessive methane formation. The COMBOCARE unit has the potential to distinguish between these sites and provide valuable technical information mechanistically about the reaction. The ethanol steam reforming reaction can be investigated at pressure, which is of significant interest because high-pressure operation allows purification of the hydrogen produced by membranes or pressure swing adsorption. Moreover, the Raman capability with this unit will provide important information about the conditions surrounding and the nature of carbon formation.

During FY 2008, we successfully demonstrated the high-throughput operando (HTO) system that was launched at EMSL. For the first time, a prototype HTO reactor has been demonstrated to allow concurrent, multiple catalyst evaluation and characterization under *operando* reaction conditions. This reactor allows simultaneous product analysis by Fourier transform-infrared (FT-IR) imaging and permits studies of catalytic mechanisms on catalyst surfaces by *in situ* Raman spectroscopy for six reaction channels. The number of reaction channels in this prototype HTO reactor can be easily scaled up. The results of this novel technique have been published in the *Review of Scientific Instruments*.

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 FT-IR 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 (0-7%) 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 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*.

Design, Synthesis and Testing of Novel High Temperature Sorbents for Removing Mercury Species from Coal to Liquids Process Streams

Glen E. Fryxell, Kent E. Parker, Richard Skaggs

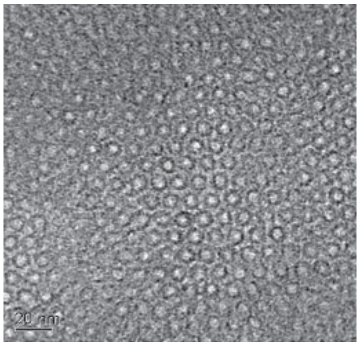
◆ Due to the nature of the coal-to-liquid process, mercury (Hg) must be sequestered at elevated temperatures to avoid energy penalties associated with cooling the process stream to remove the Hg, and then reheating it for the Fisher-Tropsch (F-T) process. Existing sorbents (e.g., sulfur-impregnated activated carbon) are not capable of capturing Hg under these conditions. New cost-effective sorbent materials need to be developed to address this need. ◆

Coal gasification is a high temperature process (400-1600°C, depending on the type of gasifier). Most of the heavy metal contaminants found in coal will be trapped in the slag/ash as their corresponding oxides or silicates. However, the unusually low boiling point (357°C) and its ease of reduction to the metallic state mean that Hg is easily volatilized. The net result is a mixture of CO, CO_2, H_2, and steam at elevated temperature contaminated with Hg. The F-T process is carried out at an elevated temperature (typically 250-300°C) over heterogeneous catalysts (commonly Fe- or Co-based) to make liquid hydrocarbon fuels from the coal-derived syngas. Hg can poison these catalysts and contaminate the fuels made by the F-T process. Currently, Hg capture is performed using activated carbon, which works well at temperatures below 100°F, but above 160°F and in the presence of water (one of the components of syngas), Hg removal cannot be consistently achieved, therefore requiring that the process stream be cooled to remove the Hg. This is energetically expensive.

The aim of this project was to design, synthesize, characterize, and evaluate novel high temperature sorbent materials for the efficient and selective capture of Hg under conditions relevant to coal-to-liquids conversion processes (i.e., vapor phase separations from a syngas matrix and recovered water from the dewatering process) and performance testing of novel sorbents. The ultimate goal is to reduce or eliminate Hg emissions from these processes and to recapture the water and purify it for process re-use. In the year 2000, freshwater withdrawals nationally for power generation (primarily cooling) were in excess of 136 billion gallons per day, only slightly less than withdrawals for irrigation. Water neutrality is of critical importance to the future of the coal power industry, and the ability to “close the loop” on process water may well be the deciding factor in whether a new plant is licensed for operation. This requires effectively scrubbing the recaptured water of Hg to avoid contamination of the product stream and/or catalyst poisoning.

The testbed was designed to allow for Hg concentration to be varied from 100 nanogram/m^3 to as much as 3000 microgram/m^3, the test gas to be varied, humidity to be controlled, and temperature to be varied from room temperature to 300°C. The Hg source was a PSA Hg vapor generator, and continuous real-time analysis of the effluent was carried out using a Lumex RA-915+ Mercury analyzer with a sensitivity of 2 ng/m^3 in the vapor phase. For a sorbent to be thermally stable at 300°C, it cannot be built around any thermally delicate components (e.g., alkyl tethers, unstable functionality); therefore, thermally stable heteroaromatic structural units offer significant advantages for this application. Thus, a primary focus of this project was to design and test various high surface area nanoporous sorbent materials built around heteroaromatic functionality.

To make the thiophene SAMMS, a pre-hydrated sample of mesoporous silica (MCM-41; 759 m^2/g, 35 Å pores) was treated with 2-thienyltrichlorosilane (estimated surface population of 2-thienylsilane was ~1.5 silanes/nm^2). The thermal stability of thiophene SAMMS was evaluated using thermogravimetric analysis, which revealed under 4% weight loss between 150 and 800°C under a N_2 atmosphere, confirming the thermal stability of thiophene SAMMS under the target conditions (i.e., ~300°C). Testing over the temperature range of 100-300°C revealed very little binding affinity for elemental Hg. Disulfide SAMMS were also made and tested. While they were found to have modest affinity for elemental Hg at 100°C, the SAMMS had insufficient thermal stability for application at the higher temperatures tested.

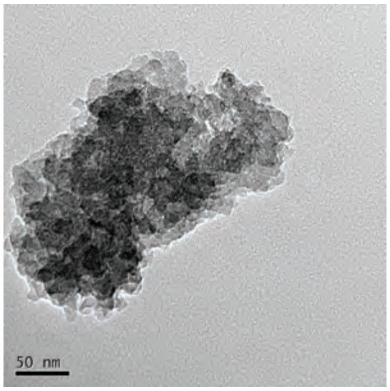


TEM of S-FMC.

Sulfur-functionalized mesoporous carbon (S-FMC) was prepared using SBA-15 as template and 2-thiophene methanol as the reactive monomer. The S-FMC obtained from this process was found to have highly ordered hexagonal pores and a basal *d* spacing of approximately 9.0 nm. The surface area was found to be in the 1400-1900 m^2/g range, and sulfur content varied from 4.4 to 7.2%, both dependent on carbonization temperature. S-FMC has excellent thermal stability; affinity for elemental Hg was good up to 200°C, dropping off at

250°C and virtually zero at 300°C. The microporosity of the S-FMC sorbent is clearly superior to the meso-porosity of the silica-based sorbents for capturing elemental Hg.

To find a cost-effective analog to S-FMC, this project undertook an effort to modify activated carbon chemically. Sulfenylated activated carbon was quickly and easily made from inexpensive starting materials, had a surface area of 1050-1270 m^2/g, and was found to have an S loading of as much as 13.4%. It was thermally stable up to ~250°C, above which temperature it began to lose its S functionality. It was found to have similar performance as an Hg sorbent to the S-FMC up to about 230°C. Other chemically modified activated carbons were made, tested, and found to have promise as Hg sorbents up to at least 250°C.



Activated carbon decorated with metal nanoparticles.

Activated carbon was also decorated with metal nanoparticles to evaluate their efficacy for capture of Hg vapor through amalgamation. The ease with which a metal forms an alloy is related to the metal's atomic radius and electro-negativity. The atomic radius of Hg is ~1.50Å, and its Pauling electronegativity is 2.00. Inspecting the properties of the other metallic elements, by far the best fit for matching these values is found with Bismuth (Bi atomic radius is ~1.60Å, and Pauling electronegativity is 2.02). We made and tested Bi nanoparticles on activated carbon and found only modest affinity between 100-250°C. Above that temperature, these materials failed (Bi melts at ~270°C).

As a part of this project, an extensive literature search was carried out on the subject of Hg speciation in coal. Of particular interest to this project was the speciation of Hg in coal derived syngas. A report was compiled summarizing these findings.

Discovery of Novel Volatile Organic Metabolic Signatures for Early Immune Response or Inflammatory Conditions

Jon H. Wahl, Nathaniel Beagley, Alan R. Willse, Kristin H. Jarman

◆ This project developed a novel comprehensive method for discovery of volatile organic compounds for signatures of early immune response to a biological pathogen and discovered unique chemical signatures from volatile components/odors. We determined the appropriate signature(s) and offer a methodology that can be used in large public events, facilities, or other arenas for rapid screening to help locate suspects or victims. ◆

The importance of odors in relation to human health was understood by ancient medical practitioners who commonly diagnosed human diseases by the smell of body odor. This same type of diagnostic procedure can be used to evaluate what a subject has been in contact with or infected by through the various chemical markers emitted by the body. Odor analysis has major advantages because it is noninvasive, represents minimal risk to personnel collecting the samples, and lends itself to frequent sampling. These markers may be odorous or non-odorous compounds, qualitative or quantitative in detection, and are likely to be a trace component(s) among the thousands that are physically emanated and collected against ambient background. Due to the extreme component complexity of such samples, comprehensive two-dimensional gas chromatography-mass spectrometry (GCxGC-MS) will be used. In general, the entire volatile compound map needs to be screened because neither the type, number, nor amount of components is known *a priori*. The complexity of these samples and the amount of data present serious data analysis challenges. As a result, this project will develop statistical and data analysis tools to aid the discovery of volatile metabolic biomarkers. This work will advance the state-of-the art in analysis of hyphenated chromatography data.

While the majority of body odor from humans is emanated via sweat and skin emanations, the body odor of mice and other rodents is linked to urine odors. Hence, initial studies and development of the analytical tools for biomarker discovery will be carried out with animal urine samples linking with other ongoing animal studies. Once analytical tools are developed and demonstrated on model systems, this toolset can be applied to other zoonotic or human infectious diseases. Transitioning to the next level in biomarker discovery will require state-of-the-art analytical tools with advanced data extraction and analysis tools.

The FY 2008 work for this project focused on examining the results obtained with the common disease model *Francisella tularensis novicida* (*F.t.n.*) in collaboration with the University of Washington. In this study, bronchoalveolar lavage fluid was collected from mice exposed to a variety of pathogens and controls; phosphate buffer solution, lipopoly-saccharide, *Pseudomonas aeruginosa*, attenuated *F.t.n.*, and *F.t.n*. The volatile headspace of these samples was then analyzed by GCxGC-MS. Because some samples arrived thawed (others did not) and at least two samples corrupted the separation columns, the effects of these variables confounded the preprocessing and overall data analyses.

As such, work in the past year focused on further upgrades, improvements of, and refinements to the algorithm(s) needed to process the raw GCxGC-MS instrument data files into peak tables from both the total and single ion chromatograms. These peak tables were required for the final statistical analysis of the study; this data processing was key to the future usability of this and other hyphenated analytical approaches. To test more fully and evaluate the preprocessing approach, we examined the algorithm on various in-house data sets, including studies from several different types (i.e., *F.t.n.*, carbohydrates). These data sets served to test the software for problems as it processed data with fundamentally different characteristics and tune the input parameters of the algorithms to optimize them for the different data types. Problems were found, so correction and adjustments (some minor, some major) were made to the algorithm. Major examples were as follows:

- Software bugs were identified, fixed, and the fixes tested
- The peak selection algorithm was replaced with a more robust approach
- For the single ion chromatogram analysis, our approach of combining all single ion chromatograms into a single result was found to lose information, so an individual ion-by-ion analysis approach was taken.

Cross-sample alignment of peaks was determined to be the primary remaining gap in the analysis of GCxGC-MS data. Some preliminary methods were explored to generate ideas for solving this problem in future research projects. Further development of the statistical tools to aid in data analysis will produce a user-enabled software tool for the chemist. These tools are applicable to many critical needs for threat-agent characterization and discovery of early markers of infection, which ultimately can be used for detection.

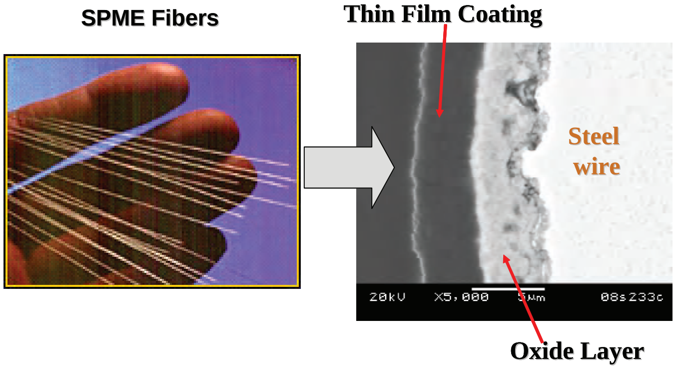
Enhanced Explosive Signature Capture via Selective Collection and Preconcentration Chemistries

R. Shane Addleman, J. Timothy Bays, Glen E. Fryxell

◆ This research aims to develop novel, functionalized nanomaterials and test them 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. ◆

Detection of explosive vapors is difficult because most explosives have low vapor pressures and/or are sealed in a container, limiting access to any signature compounds. However, as demonstrated by dogs, explosives detection via vapors is viable. Current atmospheric detection techniques are prone to false positives because they have poor selectivity and insufficient sensitivity. Improving sample cleanup through selective preconcentration of explosive signature vapors will lead to enhanced detection sensitivity and accuracy. Preconcentration techniques are ideally suited to serve as a "front end" for detection systems that separate and examine volatile materials from the air. Results derived from similar preconcentration efforts indicate the possibility of achieving a million-fold increase in analyte concentration yet maintaining the throughput, reliability, and reversibility necessary for the rapid screening and detection of improvised explosive devices.

This project is an effort to develop and evaluate novel functionalized nanomaterials and demonstrate effective, selective capture of volatile airborne explosive signatures. Upon completion of this work, we will have gained an understanding of the impact of nanostructure and surface chemistry upon collection of low-volatility explosive signatures. Our goal is to develop materials for the capture of explosive vapors in the air. To achieve this goal, our research is focused on the design and synthesis of materials for the selective and reversible adsorption of explosive vapors (specifically, 2,4,6-trinitrotoluene [TNT], 1,2-dinitrotoluene [DNT], and 1,3,5-trinitro-1,3,5-triazacyclohexane [RDX]) and the testing of materials to evaluate their relative affinity for explosive vapors (specifically, TNT, DNT, and RDX) relative to activated carbon.



During FY 2008, our work synthesized mesoporous materials with over 80 unique surface functionalities and tested them against standard commercial materials that were loaded from solution with known quantities of DNT, TNT, and RDX. After loading, samples were subjected to thermogravimetric analysis, which measures weight loss as a function of temperature. Thermal desorption temperatures for each explosive were recorded as was thermal decomposition of the surface monolayer. Data derived from our FY 2008 work indicate that thiophenyl rings bound directly to the silane surface have superior thermal properties, making them thermally robust and still able to bind strongly yet reversibly to the explosives.

These materials and others were applied as surface coatings to solid phase microextraction (SPME) fibers and glass coated wires. The coated SPME fibers are routinely used as a method for environmental sampling. The surface layer selectively adsorbs a class of analytes when the fibers are exposed to either liquids or gases, put into a thermal desorption gas chromatograph, and read out. This approach is convenient in that the small amount of material does not need further dilution for analysis. Selectively coating a glass wire provides the possibility of screening and preconcentrating large volumes of air by selectively adsorbing the analyte from a complex matrix and thermally desorbing the analyte for further preconcentration into a smaller gas volume. As a mesh, the coated wires would also be responsive to explosives, allowing particulates to stick and thermally desorbing the explosive material as a gas. We have demonstrated proof-of-concept for both approaches.

During FY 2009, our research will focus on consolidating and improving gains achieved during FY 2008. Developing a better understanding of our results and combining chemistry concepts with the form factors will ultimately lead to development of a better system. Careful combination of the physical structure with chemical surface should provide highly effective, selective preconcentration of desired explosives signatures with self-assembled monolayers on mesoporous supports. Development of such materials will be an iterative process and will depend on lessons learned at each testing step. Once select materials are developed, they can be adapted to a wide range of analytical systems. Out-year work, which will depend upon the results obtained, will include adapting effective capture materials into relevant microstructures and macrosystems.

Fundamental Investigations of Heterogeneous Catalysis Using Steady-State Isotopic Transient Kinetic Analysis

Robert S. Disselkamp, Janos Szanyi, C. Tom Campbell

◆ This project developed a unique capability for detailed research and development of heterogeneous catalysis. Researchers designed and constructed an apparatus to probe in situ adsorbed reactants/intermediates/products on catalyst surfaces while simultaneously measuring reaction kinetic parameters. The resulting novel apparatus will be applied to develop microkinetic models of catalytic reactions. ◆

Catalysis is widely used to modify and increase the reaction rate pertinent to industrial processes. The determination of the mechanism(s) of a catalytic reaction is crucial to improving current catalytic processes that lead to energy and resource conservation. Among the most common recommendations from researchers in mechanistic catalysis science is the development of methods with which to study catalytic chemistry as it occurs. Critical to these methods is the ability to make simultaneous measurements of kinetic and spectroscopic characteristics under actual catalyst operating conditions using operando methodology that combines the evaluation of structure and catalytic performance (activity, selectivity) in a single experiment. For this reason, there is renewed emphasis on studies of the reaction dynamics (kinetics and mechanisms) of catalytic processes coupled with new capabilities to probe spectroscopically the catalyst's microscopic chemical and physical properties during the catalytic process.

Many think that United States energy needs during the next few decades will be met only by a carbon-based economy (e.g., fossil fuel energy supply). This may arise from continued fossil fuel combustion chemistries or a switch to a hydrogen economy, where fuel cells become more prevalent using hydrogen from fossil fuels in fuel cells, netting an approximately 50% energy gain over direct combustion processes. In a hydrogen economy, however, there are substantial hurdles in the catalytic processes that generate hydrogen from fossil fuels such as ethanol or coal. These include fuel steam reforming of oxygenates to generate hydrogen, partial oxidation of carbon monoxide in the presence of excess hydrogen (PROX), and water-gas shift chemistries.

The specific aims of this project were to develop a new capability for performing state-of-the-art transient kinetics measurements coupled with simultaneous in situ spectroscopic characterization of the species transiently present on the catalyst surface during a catalytic process. In addition, we determined the mechanisms and kinetic parameters (activation energies and prefactors) for the elementary steps in three reactions that are industrially important with respect to hydrogen economy and that share common transition metal catalysts (platinum and nanoparticle gold) and many common elementary steps: water-gas shift, preferential oxidation of carbon monoxide in the PROX, and steam reforming of small oxygenates. Under this project, we constructed an apparatus capable of fast time response measurements (~1 second) of infrared spectra of catalyst adsorbed and gas phase species and mass spectrometric diagnostics of reactor effluent concentrations of rapidly switched gas feed inputs. This enables catalytic reaction mechanisms to be proposed to fit data and microkinetic models to represent macroscopic processes. When developed, these models will fully explain the kinetic processes, enable understanding necessary for improved catalysts, enable researchers to consider how reaction conditions affect activity and selectivity, and identify optimum catalyst operating conditions in important hydrogen production reactions of interest. Improvements by 1% in reactions could save millions of dollars annually, improve fossil fuel use efficiency, and minimize environmental impact.

During 2005 and 2006, we constructed the steady-state isotopic transient kinetic analysis (SSITKA) apparatus that contains a reactor with heaters, Fourier transform infrared and mass spectrometer, and gas handling equipment in an integrated unit. We studied carbon dioxide adsorption on an alumina catalyst, the results of which will be published in *Review of Scientific Instruments*. This work enabled a thorough testing of the apparatus by examining gas adsorption onto a catalyst support material. We also studied reverse water-gas shift reaction on a copper/alumina catalyst. We expect that this work will lead to an understanding of reaction rate-determining steps in water-gas shift reaction.

Work performed during FY 2008 included detailed SSITKA and titration studies of methanol and deuterated methanol syntheses on copper/silica catalysts. This work represented the first time surface adsorbed formate and methanol product have been detected simultaneously, enabling never before possible details of the catalytic reaction mechanism. Our measurements have illustrated that it is not hydrogenation of formate that leads to methanol production but minority surface species comprising ~0.1% of a monolayer hydrogenated to methanol. We measured the turnover frequency versus temperature-yielding activation energies, titrated surface formate with water, and observed significant methanol production, details of which we are just now beginning to understand. Obtaining high-profile publications from this work was the focus of FY 2008 efforts.

Fundamental Understanding of Carbohydrate Catalysis in Ionic Liquids

Z. Conrad Zhang, James A. Franz, Donald M. Camaioni, David L. King, Guosheng Li, Yu Su, Heather M. Brown, John L. Fulton

◆ Cellulose is the most abundant renewable carbon source available on Earth, yet its use in fuels and chemicals is limited by its recalcitrant nature. By combining applied combinatorial methods with fundamental science, this project is developing knowledge in the catalysis of cellulose to products and fuels, thereby mitigating the national dependency on petroleum-based fuels. ◆

The compound 5-Hydroxymethylfurfural (HMF) is a versatile biomass-based platform that can be used to synthesize a broad range of chemicals and fuels that are currently derived from petroleum. In addition, fuels derived from HMF using chemical processes are potential alternatives to ethanol obtained by fermentation processes. Although fructose has been the preferred feed for optimal HMF yield, it is clear that large-scale sustainable use of HMF will require lignocellulosic biomass as feed. Such use necessarily involves depolymerization of cellulose to form glucose, the building unit of cellulose, followed by conversion of the glucose to HMF. Although we recently reported a catalytic system to convert glucose efficiently to HMF, it is the depolymerization process, which involves decrystallization followed by hydrolytic cleavage, that has been the primary bottleneck limiting energy-efficient and economical utilization of cellulosic biomass. At this stage of the project, we report an unprecedented pathway that eliminates this final hurdle and enables cellulose depolymerization and glucose conversion to HMF in a single process under mild conditions.

Because cellulose depolymerization has been a particularly daunting challenge for energy-efficient and cost-effective use of the biomass as a sustainable resource, this project aims to improve the understanding of its fundamental aspects using novel tools to generate fresh ideas about how to address cellulose depolymerization. For FY 2008, we focused on the chemistry and mechanism of mixed-metal chloride catalysts in ionic liquids, the scope of which is broad. High-throughput discovery tools will continue to be used for the screening of multiple mixed-metal chlorides in ionic liquids. The types of ionic liquids as solvents will also be investigated.

We are taking a unique approach that merges combinatorial methods to screen and develops new catalysts and solvent systems with fundamental studies of the cellulose conversion processes. Our objective is to provide new technologies and expand the basic understanding that will allow cellulose to be used as a replacement for petroleum. We will also establish technically how high-throughput (combinatorial) methods and fundamental science can complement one another in solving complex problems.

During 2008, we found an unprecedented single-step pathway that depolymerizes cellulose rapidly under mild conditions and converts the resulting glucose to HMF. A pair of metal chlorides ($CuCl_2$ and $CrCl_2$) dissolved in 1-ethyl-3-methylimidazolium chloride at temperatures of 80-120°C catalyzes cellulose deploymerization and the subsequent glucose conversion to HMF with 95% selectivity among recoverable products (at 56% HMF yield). After extractive removal of HMF from the solvent, the recovered [EMIM] Cl and the catalyst continue to produce HMF in high yield. Cellulose depolymerization, which can also be catalyzed by other metal-chloride pairs such as $CuCl_2$ paired with $PdCl_2$, $CrCl_3$, or $FeCl_3$, occurs at a rate approximately one order of magnitude faster than conventional acid-catalyzed hydrolysis. By contrast, single-metal chlorides at the same total loading revealed low activity under similar conditions. We also performed preliminary fundamental studies of the low temperature cellulose hydrolysis chemistry by combining a number of characterization techniques, such as extended x-ray absorption fine structure spectroscopy, electron paramagnetic resonance, and differential scanning calorimetry. The results indicate a strong interaction between copper ions and an added second metal ion. To be sure, Cu (II) ions are reduced to Cu (I) ion in the presence of $PdCl_2$, $CrCl_2$, or $FeCl_3$ as well as cellulose.

Using high-throughput tools, a large number of transition metal chlorides in ionic liquids were evaluated for their activity in converting glucose, the building block of cellulose, to HMF, a versatile platform chemical for fuels and chemicals. Chromium (II) chloride in [3-alkyl-1-methyl-imidazolium] chloride, [AMIM] Cl, ionic liquids, was found to be the most active and selective catalyst for this conversion. The mechanism of this chemistry was further investigated, and a preliminary understanding of the mechanism was reached using model compounds glyceraldehyde and glycerol. The mechanism of cellulose decrystallization in trifluoroacetic acid was also fully investigated. It was concluded that the increased dimer concentration in low temperature is critical for the swelling and decrystallization of cellulose, which was further demonstrated to be readily hydrolyzed to glucose with largely increased rate of hydrolysis.

Fundamental Understanding of Catalytic Depolymerization of Cellulose

Z. Conrad Zhang, Heather M. Brown, Jonathan E. Holladay, Xiao-Dong Zhou

◆ Cellulose is the most abundant renewable carbon source available on Earth, yet its use in fuels and chemicals is limited by its recalcitrant nature. By combining applied combinatorial methods with fundamental science, this project is developing new knowledge in the catalysis of cellulose to products and fuels, thereby contributing to the mitigation of our national dependency on petroleum-based fuels. ◆

Carbohydrates derived from biomass, including monosaccharides and polysaccharides, provide the primary feedstock for renewable production of liquid fuels and chemical products. Cellulose can potentially meet current national energy needs if it can be converted efficiently to monomeric sugars. This requires fast, low-cost hydrolysis capability. Neither acid nor enzyme hydrolysis has been developed to an economically attractive level because of a lack of fundamental understanding of the nature of hydrated cellulose. Lignocellulosic-based biorefineries are not commercially viable today because the recalcitrant nature of cellulose makes the cost of extracting sugars exorbitant. As they pertain to liquid fuels, future domestic energy needs require that we surmount the critical barriers related to depolymerization of cellulose to easily fermented sugars (i.e., glucose).

The barriers for cellulose are unique to other carbohydrate fractions such as starch and hemicellulose. Although cellulose can be hydrolyzed by a variety of means such as enzymes and acids, these methods are problematic. Enzyme-catalyzed cellulose hydrolysis is highly selective but very slow, requiring the collection of numerous enzymes and is simply too expensive to be practical at the current level of development. Acid hydrolysis can be relatively fast at elevated temperatures but is not selective, producing significant amounts of by-products that can be toxic to downstream fermentations and lead to significant losses to the yield of desired sugar products.

Because cellulose depolymerization has been a challenge for the energy-efficient and cost-effective use of biomass as a sustainable resource, this project aims to improve understanding of its fundamental aspects using novel tools to generate fresh ideas about how to address cellulose depolymerization. We are taking a unique approach that combines high throughput (combinatorial) methods to screen and develop new catalysts and solvent systems with fundamental studies of cellulose conversion processes. Our objective is to provide new technologies and expand understanding for enabling cellulose to replace petroleum. We will establish how combinatorial methods and fundamental science can complement one another in solving complex problems.

During FY 2006, a significant body of knowledge was generated toward better understanding the bottleneck of cellulose conversion. We discovered that trifluoroacetic acid dimer molecule, which predominates at 0°C and below, effectively decrystallized cellulose to amorphous cellulose in less than 100 minutes. A most remarkable result of this treatment is that clean amorphous cellulose can be obtained and readily converted to high-yield sugars. The trifluoroacetic acid dimer served as a treatment medium and could be recycled for reuse. For the trifluoroacetic acid monomer that prevails at room temperature and above, it took weeks to decrystallize cellulose, which was trifluoroacetylated by consuming triflurorcetic acid. Nuclear magnetic resonance spectroscopy, Fourier transform infrared, and scanning-electron microscopy were applied to reveal and confirm the new cellulose decrystallization pathway.

In FY 2007, the potential of ionic liquid as a suitable solvent for catalytic conversion of carbohydrates was demonstrated. Chromium dichloride was discovered to be an effective catalyst in [EMIM]Cl ionic liquid for the selective conversion of glucose (the fundamental building block of cellulose) to hydroxymethyl-furfural (HMF), a versatile platform chemical from which fuels and chemicals can be produced. A yield of 70 percent HMF was obtained from glucose, a discovery that addressed a major challenge in chemistry for the use of cellulose-derived glucose replacing petroleum-derived chemicals for fuel and for chemical applications. We discovered a new catalyst system that is highly effective in hydrolyzing cellulose under mild reaction conditions (100 to 120°C). Typical sulfuric acid catalyzed cellulose hydrolysis takes place at much higher temperature (at or above 180°C). Cellulose hydrolysis at a lower temperature not only saves energy in process operations but also enables products to stabilize at low temperatures, thereby preventing the thermal and catalytic degradation that occur at higher temperatures.

During FY 2008 up to project completion, we achieved a fundamental understanding of the low temperature cellulose hydrolysis chemistry by combining several characterization techniques such as extended x-ray absorption fine structure spectroscopy, electron paramagnetic resonance, and differential scanning calorimetry. The results indicate a strong interaction between copper ions and an added second metal ion. Cu (II) ions are reduced to Cu (I) ion in the presence of $PdCl_2$, $CrCl_2$, or $FeCl_3$ and cellulose. A manuscript has been submitted to *Science* that reports the effect and a proposed mechanism of paired metal chlorides for low temperature conversion of cellulose to sugars or directly to HMF.

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 techniques are widely deployed for explosives detection. Most airports rely on trace detection, typically ion mobility spectrometry (IMS), for aviation security. The primary attributes that define trace detection performance, sensitivity, and selectivity can be further delineated as probability of detection and false alarm rate. Although trace detection technology is fairly mature and heavily deployed, significant opportunities for improvement still exist, specifically in enhancing selectivity to reduce false positives.

This project focuses on filling the selectivity technical gap in IMS by providing additional spectral information through the generation of a new ion species of explosives that are generated through the use of a nonradioactive discharge ionization source. In addition to increased selectivity, the new reactant ions may provide improvements to sensitivity as well the ability to suppress chemical background noise. A side benefit of this research is the use of nonradioactive ionization sources in IMS, thus eliminating the safety, environmental, and accountability concerns that result from using radioactive ionization sources.

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

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

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

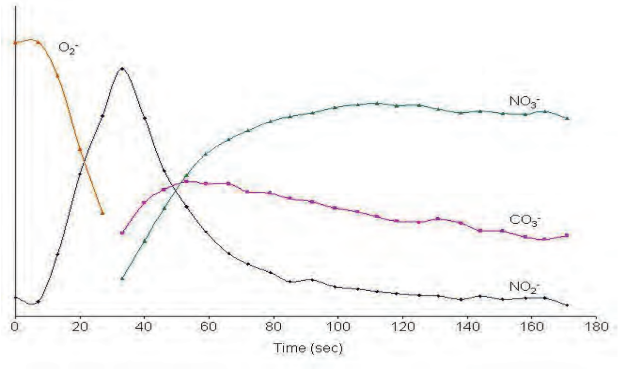
$O_2^- + O_3 \rightarrow O_3^- + O_2$ $k = 6.0 \times 10^{-10}$ cm^3/s

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

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

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

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



IMS peak intensities monitored with increasing operation time of the discharge source.

The following graph demonstrates the change in ion intensities in a mobility spectra resulting from changes in neutral vapor concentration. This experiment was intended to simulate the ionization process occurring in a discharge source by sampling the gas from a discharge in an enclosed container into an IMS while using ^{63}Ni as the source of electrons. Contained in a 500 ml bottle, the source was operated at a 50% duty cycle (5 sec on, 5 sec off). Air at 18-20 ppm H_2O passed through the bottle to the IMS at a flow rate of 40 mL/min. The x-axis in time represents the duration the source was operated and the resulting ion formations. Longer operation times resulted in higher O_3 and NO_2 concentrations.

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 the anions that are available to interact with the explosive molecules. By selecting different anions (reactant ions), new adducts with explosives will form that vary in chemical structure and size, thus producing unique explosive compound signatures. The appearance of these adducts in different locations in a mobility spectra provides an opportunity to move response away from the signature of an interfering chemical. These explosive compounds that form adducts with the chloride ion were observed in mass spectrometry to form adducts with the CO_3^-, NO_2^-, and NO_3^- anions. Ionization with nitrate reactant ions appeared to provide additional selectivity over the other reactant ions investigated. The nitrate ion has a relatively high electron affinity; in its presence, most background chemicals do not ionize, and the nitrate ion retains the charge.

During FY 2009, we will interface the source to an ion mobility spectrometer to observe peak shape and mobility values for the reactant ions and relevant product ions. Based on our findings, along with literature values of some reaction rate constants, we will propose mechanisms for the production of reactant ions and subsequent product ion formation. The spectra collected will be compared with explosives spectra generated with conventional IMS systems to quantify improvements in selectivity. Further, detection limits with the new ionization source will be estimated for sensitivity comparison.

Nanostructured Catalyst Synthesis and Applications

Jun Liu, Donghai Wang, Sheng Dai (Oak Ridge National Laboratory)

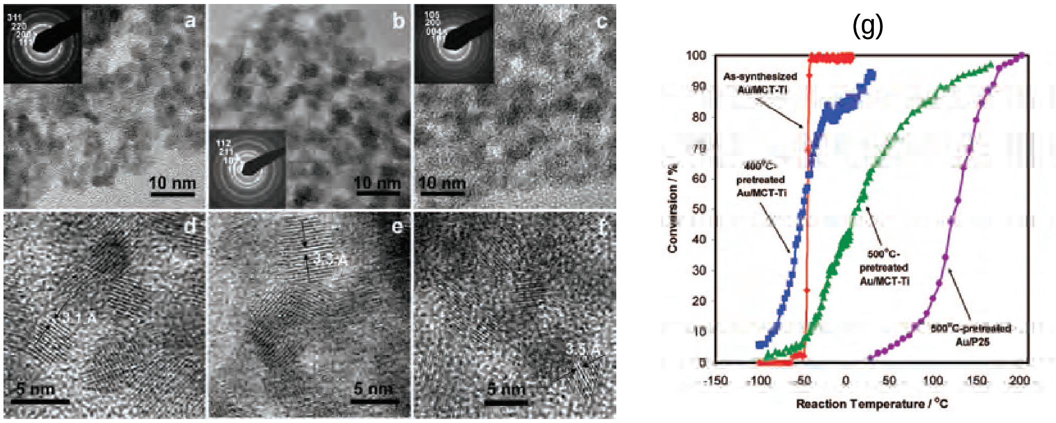
◆ The goal of this project is to develop and integrate capabilities in three critical areas of nanocatalyst synthesis: chemical synthesis, nanocrystalline catalysts, and tailored nanoporous materials. We hope to develop novel approaches to synthesize nanostructured catalysts with controlled architectures and properties from molecular to micro- and nano-scale dimensions. We will also explore energy-related applications of these materials. ◆

The principal challenge in catalysis research is to understand and control active site chemistry through manipulation of the structure, composition, and electronic properties at the catalyst surface. Heterogeneous catalysts are widely used for a range of energy and environmental applications, including selective chemical conversion, environmental remediation, photocatalytic reaction, hydrogen production, reactive absorption, fuel desulfurization, and the like. However, existing catalyst materials are structurally and chemically complex. Systematic control of the composition, surface area and chemistry, pore structure, crystallinity and the location and distribution of the catalytic sites, rigorous structure-function relationships of the catalytic properties, and atomistic understanding of the chemical transformations over the catalysts remain primary challenges for catalyst synthesis.

We developed a novel solution growth of metal oxide nanocrystals within an organized surfactant matrix into three-dimensional nanostructured frameworks with tunable porosity. We selected anionic sulfate/sulfonate surfactant that can strongly interact with metal cations such as Ce^{3+}, Sn^{2+}, and Ti^{3+} to form mesostructured metal cation/surfactant composite. To produce mesoporous crystalline transition metal oxides, metal cations were linked to form M-O-M bonds via an oxidative hydrolysis-coupling reaction in the presence of the anionic sulfate surfactant, which strongly interacts with metal cations or oxide species and serves as a pore-directing agent. The nucleation and growth of stable nanocrystalline dioxide are formed by oxolation via oxidation of metal cations by an oxidizing agent (i.e., hydrogen peroxide) and the slow release of hydroxyl ions owing to thermal decomposition of hexamethylenetetramine in aqueous solutions. We have grown high-surface area crystalline transition metal oxides (HCTs), including CeO_2, SnO_2, and extended to mixed oxide $Ti_xSn_{1-x}O_2$, which are designated as HCT-Ce, HCT-Sn, and HCT-TS, respectively.

The high-surface area mesoporous crystalline CeO_2 is loaded with Au nanocatalysts via deposition-precipitation methods for catalytic testing of both low-temperature CO oxidation and WGS reaction. The 500°C-aged Au/HCT-Ce catalysts were very active, achieving 50% conversion around –25°C in CO oxidation.

Stability tests showed that the catalysts could maintain a CO conversion rate higher than 90% for 70 hrs at room temperature. The 500°C-aged Au/HCT-Ce catalysts are also active in WGS reaction, obtaining 75% CO conversion at 296°C in WGS reaction. Stability tests also showed that the catalysts in WGS reaction could maintain a CO conversion rate higher than 65% for 70 hrs at 296°C. The catalytic results suggested that HCT-Ce supported gold catalysts are much more resistant to high-temperature (i.e., 500°C) aging and still exhibit high activity with sustained on-stream stability in both low-temperature CO oxidation and WGS reaction.



TEM images of calcined HCT-Ce (a), HCT-Sn (b), and HCT-Ti/Sn (c). The inset shows selected area electron diffraction pattern corresponding to fluorite, cassiterite, and anatase polycry-stalline structure. High-resolution TEM images of CeO_2 *(d),* SnO_2 *(e), and anatase (f)* TiO_2 *nanocrystalls in mesoporous framework of HCTs. (g) Catalytic performance of Au/MCT-Ti for low-temperature CO oxidation: light-off curves of as-synthesized Au/MCT-Ti, 400°C-pretreated Au/MCT-Ti, 500°C-pretreated Au/MCT-Ti, and 500°C-pretreated Au/P25.*

n-Doped Electron Transporting System for Top-Emitting White Organic Light-Emitting Devices Applications

Linda S. Sapochak, Daniel J. Gaspar, Glen E. Fryxell, Jonathan L. Male

◆ In order for organic light-emitting devices (OLEDs) to meet the needs of the nation in increasing the efficiency of buildings and lowering energy usage, many advances must be made in efficiency technology and cost compared with current devices. We are working on an electron-injection system to reduce operating voltage and improve organic light-emitting device efficiency through chemical modification of one electrode in an organic light-emitting device. ◆

Design of new material systems to improve electron injection is highly dependent on device configuration and emission color. For practical white light applications, the bottom-emitting OLED configuration fabricated on indium tin oxide (ITO) coated glass (or plastic) is not a viable low-cost solution due to the high cost of indium. A white OLED panel is likely to be fabricated in a top-emitting OLED configuration on lightweight metal foil. Further, all approaches to generating white light require a blue-emitting component. In contrast to current research efforts in electron injection and *n*-doping, our system uses solution processing to achieve better control of the chemistries between electron transport materials and electrode modification chemistry without complications arising from direct metal deposition on top of organic layers.

This project seeks to develop an electron injection system comprised of a self-assembling chemical species incorporating electron-rich moieties that efficiently transfers charge to an OLED electron transport material. The system is designed to be compatible with top-emitting blue OLEDs. We will introduce a novel approach to achieving organic molecular *n*-doping by solution processing to lower operating voltages of organic light-emitting devices in a practical device configuration for low-cost solid state lighting applications. The co-development of our newly developed *n*-doped system and top-emitting technology in our laboratories will be a significant advancement in solid state lighting organic light-emitting devices technology. The proposed work and potential new areas of research such as nano-grafting of SAMS for pattern fabrication will strengthen our core capabilities in solid state lighting.

The project has been executed through a combination of computational and synthetic chemistries and thin-film deposition. The computational chemistry was used to direct the modification of the electro-rich complexes in order to ensure the electronic structure would remain favorable for charge injection. Two approaches were employed for the self-assembled film. In the first approach, electron injection chemistry was generated on the surface through stepwise synthesis of the molecule while anchored to the Ag electrode material. In the second approach, other versions of the electron injection material were synthesized, and a thin film was formed using standard self-assembly techniques. Photophysical and surface chemical analyses were used to characterize both synthesized materials: the generated thin films and the interaction between the electron injection and transport material.

Our results indicate that we have achieved several of our goals. First, computational studies were used to determine the monolayer height in order to confirm layer thickness determined by ellipsometry. Second, proposed chemical modifications would not negatively affect the molecular electronic structure. The computational studies also pointed to two particular phosphine oxide electron transport materials (PO15 and $PO15O_2$) as good test molecules for a non-interacting species (PO15) and a suitable acceptor ($PO15O_2$). Second, we showed through mechanical mixing that the electron transport materials behaved as expected with the electron-rich injection material: the PO15 showed no interaction, and the $PO15O_2$ exhibited new infrared absorption features attributable to this interaction. Third, we achieved our goal of generating a self-assembled thin film by stepwise synthesis on the surface. Finally, we succeeded in synthesizing an alternative self-assembly precursor should subsequent device studies indicate the initial linkage is not robust enough under processing or operational conditions.

The next work will be the refinement of the self-assembly materials and tighter control over layer growth. This will be followed by the generation of devices to down-select the optimal means to tether the *n*-dopant and demonstrate the utility of this approach in decreasing OLED operating voltage. Key experiments will examine the effects of *n*-dopant concentration and vertical positioning within the electron transport layer. The electron-injection system will then be incorporated into a working blue OLED, and characterizing the electrical and light emission characteristics of the device will be facilitated.

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, and inexpensive catalysts for the electrochemical production and utilization of hydrogen (H_2) will play an important role in the development of fuel cells and electrolyzers required for a hydrogen economy. The existence of hydrogenase enzymes based on nickel and iron indicate that fast, efficient nonbiological nickel and iron catalysts for hydrogen production can be developed. This project will build on previous research in which nickel complexes containing pendant nitrogen bases have been shown to be catalysts for H_2 oxidation with very low overpotentials. However, these catalysts are not fast. This project will probe specific structural features of this class of catalysts in an attempt 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.

This project will provide a fundamental scientific understanding of H_2 oxidation/reduction structure catalysts that allow the development of optimized materials that will operate at much higher rates than naturally occurring catalysts. The work will provide understanding in an area of key technological importance, the production and reduction and oxidation of hydrogen, processes essential to the technology of the storage and conversion of electrical energy in small molecules. Our specific aim is to develop an electrocatalyst based on nickel complexes that have performance characteristics comparable or superior to those of hydrogenase enzymes and/or platinum metal. This will be achieved by a rational development of these catalysts based on an understanding of the structural features controlling the thermodynamics and kinetics of proton and hydride transfer reactions.

We recently reported the synthesis of a new series of nickel(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 a catalyst for the electrochemical oxidation of hydrogen 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.

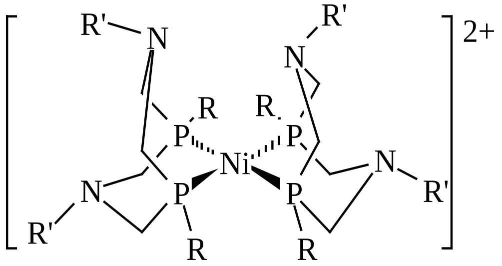
1a: R=cyclohexyl; R’=benzyl

1b: R=R’=phenyl

1c: R=cyclohexyl; R’=benzyl

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 investigated the use of some of the complexes described above for their ability to catalyze the reduction of O_2. This problem was studied in two ways. First, the reduction of O_2 using H_2 gas in the presence of different catalysts was explored using a variety of catalysts. Specifically, we studied the effect of the number of proton relays on the nature of the products produced (i.e., H_2O_2 or H_2O). Preliminary studies in our laboratories with nickel-phosphine systems support the important role that proton relays can play in O_2 reduction.

In the presence of D_2 and oxygen, the nickel complex $[Ni(P^{Ph}_2N^{Bz}_2)_2]^{2+}$ shown in **1c** has been found to catalyze the reduction of oxygen to D_2O on the basis of ^2D NMR studies, showing the formation of D_2O in CH_3CN (δ 2.1). In contrast, $[Ni(P^{Ph}_2N^{Bz}_2)(dppp)]^{2+}$, where dppp is bis (diphenyl-phosphino) propane catalyzes the reduction of O_2 to form D_2O_2 (δ 6.1 in the ^2D NMR spectrum[131]). In addition, cyclic voltammograms of $[Ni(P^{Ph}_2N^{Bz}_2)_2]^{2+}$ show large catalytic waves in the presence of O_2 and protons, waves that have catalytic currents at least 50 times greater than those of the catalyst alone. This implies a very high turnover frequency for electrocatalytic O_2 reduction. However, $[Ni(diphosphine)_2]^{2+}$ complexes with no relay at comparable overpotentials exhibit very low or no activity. These results clearly demonstrate that proton relays play an important role in O_2 reduction and that the number of relays may determine whether two- or four-electron reduction products are observed. These preliminary results are quite encouraging regarding the important role that proton relays can play in O_2 reduction.



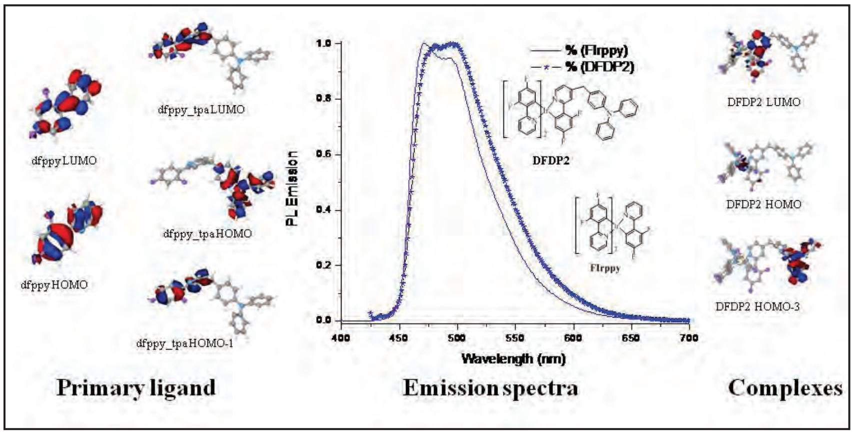
Novel Emitter Materials for Organic Thin Film Electroluminescence

Asanga B. Padmaperuma, Philip K. Koech, Linda S. Sapochak

◆ Organic-based materials are versatile building blocks for future technologies that can significantly increase energy-conversion efficiencies of solid-state lighting and display devices. Practical commercial applications require high efficiencies and stabilities that can be obtained only by the proper balance of electronic charges. ◆

DOE is working to accelerate advances in solid-state lighting for general illumination. Organic light-emitting device (OLED) technology is a pivotal emerging technology that promises to assist fundamentally in future lighting energy needs. A major obstacle in developing efficient, stable OLEDs necessary for white light is a difficulty in achieving balanced charge injection and transport into the active emissive layer of the device. An OLED is composed of thin-film organic layers that inject charges (electrons and holes) into the layers under applied bias. The electrons and holes recombine in the emissive layer to produce light; however, organic materials have different charge transport properties (i.e., holes typically move faster than electrons). Hence, there will always be a charge imbalance that causes decreased device efficiencies and poorer lifetime. This is particularly problematic for high-energy-emitting OLEDs, which are composed of blue-emitting organometallic iridium complexes doped into wide energy gap host materials. This composite layer is necessary to prevent the iridium complex from self-quenching. However, increasing the energy gap of the host typically results in poor charge transport properties and larger charge imbalances.

The objective of this project is to design and synthesize vacuum-sublimeable organometallic iridium complexes with bipolar charge transport to achieve optimum charge balance in blue electro-phosphorescent OLEDs without self-quenching the emitter. Development of these new multi-functional emitters will increase both the efficiency and lifetime of high-energy OLEDs.



The three parameters required to design tailored organometallic charge-transporting phosphors are: 1) triplet exciton energy (E_T), 2) energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and 3) reorganizational energy (λ) of the hole-transporting moiety (HTM). Since the focus is on optimizing blue OLEDs only chromophores with $E_T >$ 2.7eV were considered. The HOMO and LUMO energies and the λ of HTM units were predicted using computational capabilities established in the first year of this project. The λ results from the change in nuclear coordinates that occurs when a charge is introduced to the molecular system and from changes in the surrounding environment due to polarization effects.

Results show that derivatizing a common ligand used in blue OLEDs [2,4-difluorophenylpyridine (dfppy)] with a common HTM [i.e., triphenylamine (tpa)] does not change the energy of the states involved in emission. Time-dependent density functional theory calculations verify that HTM was not involved in the primary absorption and emission process of the complex. The predicted intra-molecular reorganization energies (λ_i) of the HTM (tpa) upon acceptance of a hole is 2.6 kcal/mol and upon attachment to the dfppy ligand, λ_i(dfppy-tpa) increases slightly to 3.3 kcal/mol, both values of which are significantly lower than the dfppy ligand itself (8 kcal/mol).

The first-generation molecule developed in the first year of this project had good electronic properties. However, attempts to sublime this molecule resulted in decomposition due to the instability of the ether linkage used to attach the carbazole moiety to the secondary ligand. Second-generation molecules were designed to achieve electronic properties similar to FIrppy but with a more robust linker group (e.g., methylene in place of ether linkage) in order to be sublimeable for device studies. A new homoleptic blue-emitting iridium complex (dFDP2) derivatized with an HTM was synthesized, and the absorption and emission properties exhibited similar emission spectrum to that of FIrppy. Absorption bands characteristic of triphenylamine were visible in the absorption spectrum of dFDP2, but this moiety did not contribute to the light emission except to broaden the low-energy side of the spectrum through vibrational coupling to the complex. Chemical analysis of the materials collected after vacuum sublimation suggests that sublimation does not lead to decomposition or chemical conversion to side products.

Preparation and Characterization of Peptide Arrays Using Soft Landing

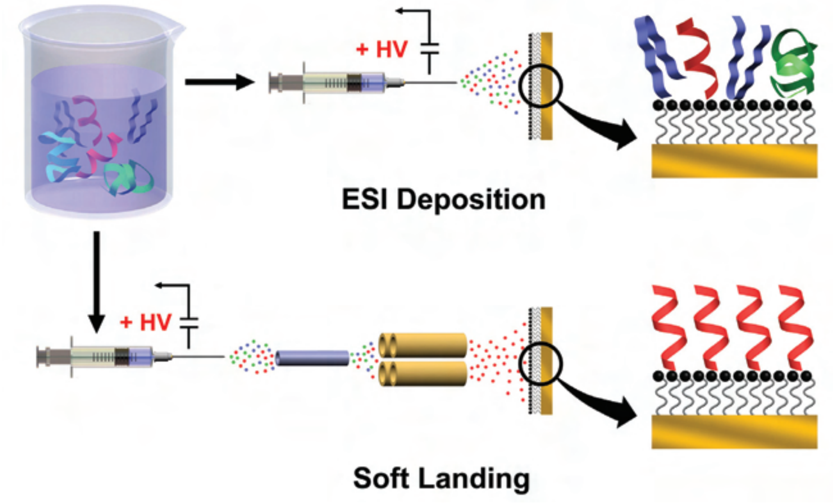
Julia Laskin, Paul L. Gassman, Peng Wang

◆ This research will provide the necessary background for the preparation and characterization of novel materials relevant for material science and biotechnology. This combination of new approaches for preparing and characterizing biological surfaces will open an entirely new field of science. ◆

Interaction of ions with surfaces is an area of active fundamental research in surface science relevant to a broad range of other scientific disciplines such as materials science, mass spectrometry, imaging, and spectroscopy. Two major processes are dominant for low-energy ion-surface collisions: reactive and nonreactive scattering of ions, and ion loss on the surface as a result of neutralization or soft landing of projectile ions. Soft landing and a related process of ion reactive landing, in which ion is covalently attached to the surface, are unique processes that occur during collisions of low-energy ions with self-assembled monolayer (SAM) surfaces. The objective of this study is to develop a novel approach for preparing peptide arrays using soft landing of mass-selected peptide ions. This research specifically focuses on reactive and nonreactive deposition of hyperthermal mass-selected peptide ions on organic surfaces.

During FY 2008, we focused on preparing conformationally-selected peptide arrays using soft landing of mass-selected peptide ions on SAM surfaces. The singly protonated Ac-A_{15}K peptide was selected as a model system for this study because ion mobility measurements and molecular dynamics simulations demonstrated that this peptide forms an α-helical conformation in the gas phase stabilized by the interaction between the protonated C-terminal lysine residue and the helix dipole. We demonstrated formation of the α-helical peptide array on an inert SAM of alkylthiol on gold and covalent immobilization of the Ac-A_{15}K peptide on a reactive SAM of N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM) with retention of the secondary structure. Because the NHS-SAM surface readily reacts with primary amino groups in proteins or peptides by forming amide bonds, this substrate has been previously used for efficient covalent immobilization of soft-landed peptides onto SAMs via the formation of an amide bond between the SAM and the amino group of the lysine side chain. SAM surfaces before and after soft landing were characterized *ex situ* using time-of-flight secondary ion mass spectrometry and infrared reflection absorption spectroscopy, which was used to obtain structural information about the soft-landed peptide molecules.

Our results showed that while the Ac-A_{15}K grafted onto SAM surfaces from solution favored the β-sheet structure, deposition of $[\text{Ac-A}_{15}\text{K+H}]^+$ ions from the gas phase resulted in formation of a stable α-helical peptide layer on SAM surfaces. It is reasonable to assume that if the conformational transition to the most stable α-helical structure of the gas-phase protonated peptide is associated with a substantial free energy barrier, it is facilitated by collisions with the background gas in the high-pressure interface of our instrument. Further, we found that soft-landed peptide molecules retained the α-helical conformation in the ambient environment for at least 20 days. Deposition of $[\text{Ac-A}_{15}\text{K+H}]^+$ onto the reactive NHS-SAM resulted in covalent immobilization of the α-helical conformation on the surface. It is remarkablethat the covalently linked peptide molecules retained their gas-phase conformation following both extensive rinsing and immersion in trifluoroethanol. This study presents a first step toward controlled immobilization of conformationally pure peptides and proteins on solid supports using soft landing and reactive landing. Our results suggest that the combination of the ion mobility separation with soft landing and reactive landing experiments could be used in future studies for conformation enrichment and the preparation of conformation-specific peptide and protein arrays.



Soft landing of mass-selected peptide ions can be used for preparation of conformation-specific peptide arrays on self-assembled monolayer surfaces. Deposition from solution results in formation of a peptide layer dominated by the β-sheet structure, whereas with soft landing, a stable α-helical peptide layer on SAM surfaces is formed.

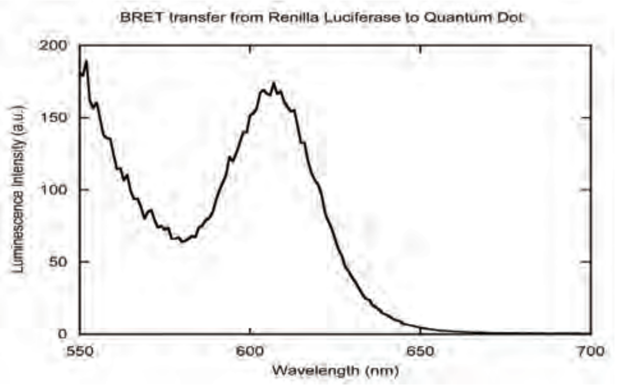
Reagent Selection Methodology for a Novel Explosives Detection Immunoassay Approach

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

◆ The goal of this research 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 antibody fragments can be used to detect small (<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) needed to solvate molecules (such as TNT) 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 homo- and heterogeneous immunoassay formats.

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 (e.g., green fluorescent protein) is measured as fluorescent emission at a different wavelength than the fluorescent protein alone. This method has the unique feature that no external excitation source is required to produce the fluorescence signal. In addition, BRET assays have the distinct 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 our efforts on using BRET-based immunoassays.



Data showing the BRET transfer from Renilla Luciferase synthesized in house to a quantum dot with an emission maximum at ~605 nm.

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, development of a methodology for obtaining specific antibody subunit pairs for open sandwich assays remains a significant challenge that we address in this work.

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). Our approach relies 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 the surface of bactreriophage. 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. The method we developed is the first that uses a high-throughput system to produce reagent pairs readily for the open sandwich immunoassay technique with FRET or BRET detection. In addition, we developed a quantum dot-based BRET reagent using both 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 the interactions of these materials in parallel with the development of the protein reagents. In FY 2009, we will continue to investigate the production of the reagents and begin to design assays that employ them for the detection of explosives and their byproducts.

Earth and Space Sciences

Assessing the Impacts of Model Resolution at the Mesoscale and Cloud Resolving Scale on Climate Simulations in the Tropics

Lai-Yung Ruby Leung

◆ Climate models are the primary research tools used to understand and project future climate changes. This project evaluates the impacts of climate models at two sets of grid resolutions that resolve mesoscale atmospheric processes and convection on simulating tropical processes to provide guidance for future climate model development. ◆

The objective of this project was to assess the impacts of model resolution systematically from cloud resolving scale to mesoscale on climate predictions, including the ability to simulate processes over complex terrain and tropical convection and examine its impacts on the environment. We proposed to perform numerical experiments using the Weather Research and Forecasting (WRF) model configured in regional/global domains with the following specific goals:

- To assess systematically the impacts of spatial resolution on tropical convection, we proposed to apply WRF at the cloud resolving scale (1, 2, and 4 km) and mesoscale (10, 20, and 40 km), respectively. At each spatial resolution, a one-year simulation will be performed over the Pacific warm pool, with large-scale circulation provided by a global reanalysis.
- To assess further the impacts of spatial resolution in the context of scale-interactions, we proposed to perform global WRF simulations for an aqua planet to investigate tropical biases. We included tropical channel domains of 36 and 12 km spatial resolution within the global WRF.

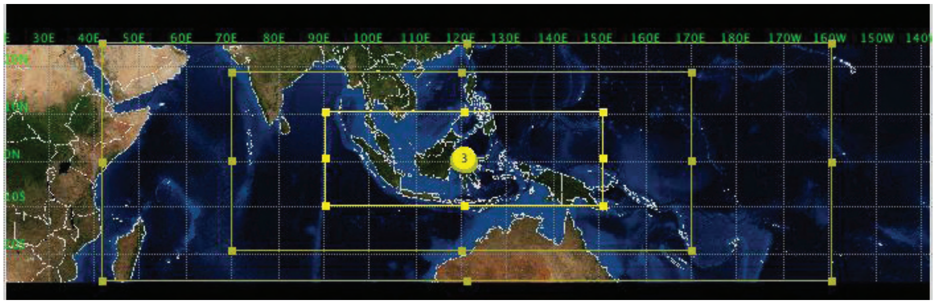
This study will provide guidance for future direction and computational requirements of climate modeling at the cloud resolving scale, with the ultimate goal of improving both the accuracy and spatial specificity of climate predictions. The latest version (3.0) of the WRF has been adapted to Jaguar (Cray XT4) at the National Center for Computation Sciences (NCCS), where we have sufficient computational resources to perform cloud resolving simulations at 1-4 km grid resolution. The fundamental strategy is first to run simulations on the largest domain (40 km grid resolution) alone and generate forcing data from the largest to the intermediate domain (20 km resolution), run simulation on the intermediate domain alone, and generate forcing data for the finest domain (10 km grid resolution) and perform simulations. These steps will be repeated for another set of three model domains at the 4, 2, and 1 km grid resolution.

Atmospheric and sea surface temperature data have been used to provide lateral and lower boundary conditions for the simulations. Since WRF version 3.0 was not thoroughly tested on Jaguar, we found several problems compiling and running the model. We tested the use of different physics parameterizations, compiler options, and atmospheric and sea surface temperature, forcing data to isolate the cause of the problems.

We also initiated work on the second task to perform a global WRF simulation on an aqua planet. This simulation included high-resolution nested domains over the tropics to study the impacts of upscaling fine-scale meteorological and cloud processes to coarser scales of motion. This task consists of three broad parts. Part 1 is the WRF model configuration as an aqua planet. The newly released global domain capability in WRF version 3 has been used as a starting point for this task. Programs written to modify WRF input files so that they resemble an aqua planet are mostly complete, with the exception of the modifications necessary for the land areas to appear as ocean. Currently, we are using an analysis from the Global Forecast System as a starting point interpolated to a flat planet. We then applied mild smoothing to the interpolated dynamical fields to maintain stability during the first several hours of model integration.

Part 2 consisted of performing a year-long simulation of the global aqua planet domain to see how it behaved without an embedded high-resolution nest. We planned to run the same configuration on Jaguar at NCCS; however, the aforementioned technical issues porting WRF to Jaguar needed to be resolved in order to perform long-term simulations.

The project ended with the close of the 2008 fiscal year. We have since solicited help from NCCS and the National Center for Atmospheric Research on issues porting WRF to Jaguar. Once these issues are resolved, we will propose a continuation of the project to perform the simulations and analysis.



Three nested domains at resolutions of 40, 20, and 10 km spacing to cover the Indian Ocean, Maritime Continent, and Tropical Western Pacific area.

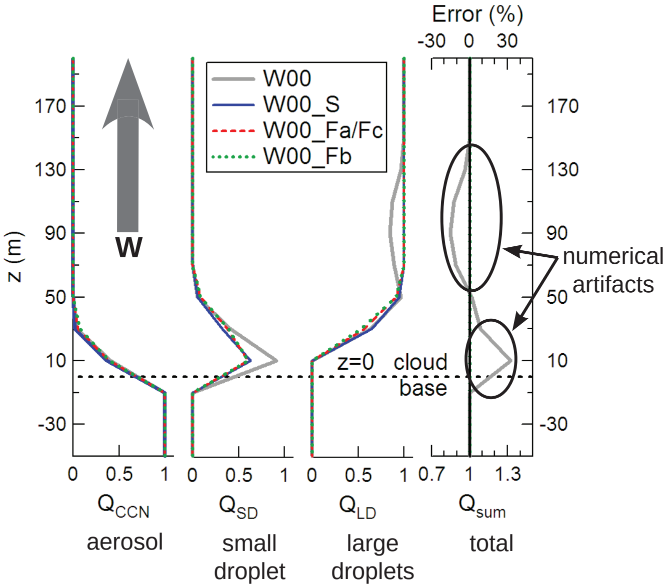
Benchmark Modeling of the Microphysical Aspects of Cloud-Aerosol Interactions

Mikhail Ovtchinnikov, Richard C. Easter

◆ One of the greatest uncertainties in predicting natural and anthropogenic climate changes arises from the inadequate treatment of cloud-aerosol interactions in global climate models. This project is aimed at advancing our understanding of cloud-aerosol interactions and improving model representation of the relevant processes. ◆

Aerosol and clouds are important components of the Earth's atmosphere and climate system and are intimately linked. Indeed, aerosol composition and spatial and size distributions determine the micro- and macrostructure of clouds. At the same time, the clouds themselves are a major modulator of these aerosol properties. The wide range of temporal and spatial scales at which cloud-aerosol interactions occur makes it difficult to predict the so-called direct and indirect aerosol effects accurately (i.e., the response of the climate system to a change in external aerosol sources).

Advection or transport of aerosol and cloud particles and substances by the moving air is one of the most important processes to be represented in spatially gridded atmospheric models of many scales from boundary layer models to global climate models. Many available numerical schemes used to simulate the process achieve a high order of accuracy but may produce undesirable oscillations near sharp spatial gradients in advected fields often encountered in atmospheric modeling (e.g., fronts or cloud boundaries). Corrections and constraints must therefore be applied to preserve positiveness of variables, such as gas and particle mixing ratios for which negative values are nonphysical. While these modifications provide the algorithms with desired properties such as positive-definiteness and improved gradient preservation, they also make these algorithms nonlinear. Consequently, any relation between tracers advected separately is not necessarily preserved. This presents a serious problem for the models in which variables derived from several tracers represent important properties.



An example of artificial redistribution (gray line) of the total concentration that resulted from advection of three categories of interacting particle types – aerosol, small droplets, and large droplets – in a cloud-like updraft. Blue, red, and green lines illustrate solutions using three different corrective procedures to the advection algorithm.

In this study, we evaluated and corrected errors introduced when conventional advection algorithms are applied to models that represent particle size distributions using a number of size categories (bins). In FY 2007, we successfully identified nonlinear monotonic constraints and flux corrections used in advection algorithms of many atmospheric models as a source of significant errors leading to local non-conservation of important integral aerosol properties, such as total number concentration of all aerosol species transported separately. We designed and performed one- and two-dimensional tests to quantify the effects of nonlinear advection algorithms on modeling cloud-aerosol interaction. A correction to the advection scheme to preserve the linear sum of bin number concentrations has also been developed.

In FY 2008, we increased the number of tested algorithms to four and developed a more accurate correction procedure. We also developed an idealized model of droplet activation and growth in an updraft to illustrate possible implications of the advection errors on simulated cloud and aerosol properties. Using these new tests, we showed that improving the accuracy of advection for individual tracers (e.g., particle concentration in a certain size range) can compete against preservation of an integrated property such as total particle concentration. While there could to be no universally optimal solution to this dilemma, the rationale is that for studying cloud-aerosol interaction, the compromise will often be weighted toward maintaining spatial distribution of total particle number (or mass) mixing ratio at the expense of perturbing spatial distributions of mixing ratio for individual bins.

The results from this project were presented at the American Geophysical Union annual meeting in December 2007 and will be published in the American Meteorological Society's *Monthly Weather Review* in 2009.

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

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

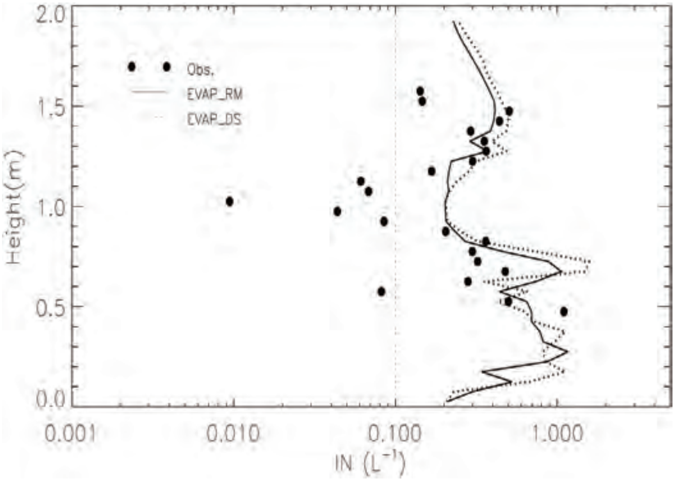
◆ One of the greatest uncertainties in predicting future climate is the effects of aerosols on cloud formation. This project will build a cloud resolving model and a set of evaluation tools that will improve our understanding of aerosol-cloud interactions and aid in the development of improved parameterizations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

There are two primary uncertainties in studying indirect effects of aerosols: the effect of aerosol on clouds and the effect of clouds on aerosol. Previously, some effort has been given to studying aerosol effects on clouds, but few have integrated that knowledge into global models. In particular, little effort has been given to studying aerosol effects on ice and mixed-phase clouds, and cloud effects on aerosols. This project will address these problems by integrating a detailed spectral bin model into a dynamic framework of a cloud-resolving model, which is the primary workhorse of the multiscale modeling framework global model. We will improve the ice microphysics scheme and the treatment of cloud effects on aerosols within the spectral bin model, which will provide a consistent framework for testing and improving new parameterizations for climate models. We will also develop a set of tools to use for model evaluation to help simulate measured quantities using model output that can be compared directly to measurements.

In FY 2007, we collaborated with Dr. Alexander Khain from the Hebrew University of Jerusalem and his research group on merging their spectral bin model, which represents one of the most advanced available treatments of cloud processes with a dynamical core of a cloud resolving model used at PNNL. We also 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 off-line on model output and facilitate validation of model results with real observations.

During FY 2008, we further developed model capabilities, focusing on improving treatments of aerosol processes. Most importantly, a direct link between aerosol properties and ice nucleation—particles that lead to the formation of ice crystals in the atmosphere—was established in the model. Ice nucleus size distribution was added as a prognostic variable to the model, with ice nucleus sources and sinks explicitly calculated. Two possible ice enhancement mechanisms – activation of droplet evaporation residues by condensation, followed by freezing and droplet evaporation freezing by contact freezing inside-out – were scrutinized by extensive comparisons with the in situ and remote sensing measurements. Simulations with either mechanism agreed well with the in situ and remote sensing measurements of ice microphysical properties. In simulations of Arctic mixed-phase clouds, these two mechanisms resulted in similar cloud properties, although ice nucleation occurred at different rates and locations. Both ice enhancement mechanisms contributed dramatically to ice formation, with ice particle concentration of 10 to 15 times higher relative to the simulation without either. It was found that ice nuclei recycling from ice sublimation contribute significantly to maintaining concentrations of ice nuclei and ice particles in this case, implying an important role of that process in maintaining the observed persistence of Arctic mixed-phase clouds.

In FY 2009, we will continue to refine the treatment of ice formation in the model, focusing our efforts on homogeneous ice nucleation at temperatures below -35°C. These processes are of critical importance 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 important climatically. We will demonstrate model performance by presenting results at a scientific conference and submitting a publication to a peer-reviewed journal describing our model development efforts and sensitivity studies.



A comparison of measured (dots) and model predicted (lines) vertical profiles of ice nucleus concentration. Each dot represents an average of all samples collected by an airborne probe in a 40-m layer. Simulations using different ice formation mechanisms are represented by two lines, resulting in similar profiles.

Development and Evaluation of a Benchmark Aerosol Chemistry, Dynamics, and Microphysics Model

Rahul A. Zaveri, Richard C. Easter, James C. Barnard, Nicole Riemer, Matt West

◆ Atmospheric aerosols (suspended fine particulate matter) are widely recognized as key elements in multiple 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 various types of particles commonly found in the atmosphere. ◆

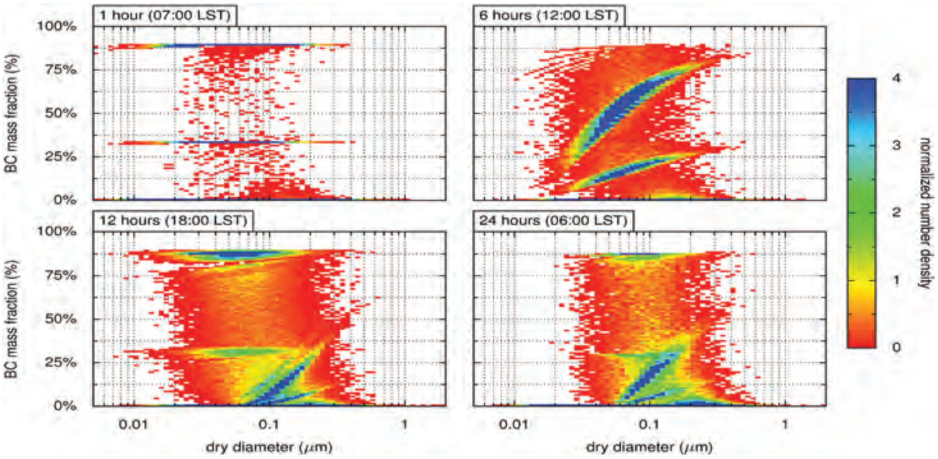
Atmospheric aerosols range from a few nanometers to a few microns and can be composed of several species such as soluble salts, insoluble dust, soot, and organic compounds of anthropogenic and biogenic origins. Primary particles emitted and particles formed via homogeneous nucleation initially exist as separate populations. Upon interacting with semi-volatile gases in the atmosphere via condensation (and evaporation) or via coagulation, these particles undergo size, morphology, and chemical composition changes and gradually become internally mixed.

Available sectional methods for aerosol aging are prone to errors due to numerical diffusion, which artificially distorts the number and species mass size distributions after condensation and coagulation equations are solved, even though total species mass is conserved. This project developed a novel aerosol chemistry, dynamics, and microphysics model that explicitly resolves and tracks the evolution of individual particles in a given aerosol population. Such a model can provide deeper insights into the roles of various processes that govern aerosol evolution than previously possible and will serve as a numerical benchmark to evaluate and improve various sectional representations for use in three-dimensional climate models.

We developed and tested the new particle-resolved aerosol model by coupling three state-of-the-art modules: 1) the aerosol chemistry module Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), which treats all the globally important aerosol species, including sulfate, nitrate, chloride, carbonate, ammonium, sodium, calcium, primary organic mass, secondary organic mass (8 species), black carbon, and inert inorganic mass, 2) the stochastic Monte Carlo particle coagulation code (PartMC), which was recently developed by University of Illinois at Urbana-Champaign collaborators Drs. Nicole Riemer and Matthew West, and 3) the shell-core aerosol optics module to treat light scattering and absorption by black carbon particles coated with soluble materials. The new model is referred to as PartMC-MOSAIC.

To test its performance, we applied PartMC-MOSAIC to an idealized urban plume case, where 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 organic carbon. 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 12 additional hours in this urban air as it advected away from the source region. By explicitly resolving more than 100,000 particles in a representative volume in this urban plume, the PartMC-MOSAIC model was able to simulate accurately the effects of coagulation and condensation on the evolution of the mixing state of urban soot particles over 24 hours (see figure).

We have analyzed the contributions of the condensation and coagulation processes in transforming externally mixed particles into internal mixtures of varying degrees. We have also investigated the evolution of aerosol optical, hygroscopic, and cloud activation properties with the particle-resolved aerosol model, and found that these properties are highly sensitive to the aerosol mixing state after 12 to 24 hours of processing. Finally, using the PartMC-MOSAIC results as benchmarks, we found that the internal-mixture assumption used in sectional aerosol models introduced significant errors in the predicted optical and cloud activation properties.



Evolution of the size-resolved distribution of black carbon mixing state.

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 urban 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 ultimately result in more efficient measures to protect citizens from daily pollutants and contaminants released 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 computational fluid dynamics modeling capability is established, a number of atmospheric sciences 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 expected from this project is the demonstration of high-resolution modeling as a tool for examining outdoor urban flows. Modeled gas dispersion from an outdoor urban release will be compared with measurements, and physical mechanisms driving the dispersion will be explored. This project will result in the development of a computational fluid dynamics modeling capability to simulate exterior urban-scale flows as well as interior duct flows and the documentation of this capability in a manuscript. The ability to incorporate building and stack geometries readily from commonly-used file formats will be developed. Simulation of an urban area as well as a simulation of a stack model will also be conducted to demonstrate the proof-of-concept.

The commercially-available STAR code has been selected to conduct these urban atmospheric computational fluid dynamics simulations. Staff at PNNL have many years of experience using this software, which has been an indispensable resource for becoming familiar with this code. Additionally, there are three main categories of accomplishments made under this project in FY 2008: 1) boundary conditions, 2) geometry, and 3) simulations.

Computational fluid dynamics simulations require appropriate boundary and initial conditions to define the modeling case. For this project, a steady-state case with standard k-epsilon turbulence closure is considered. This requires wind speed and direction as well as turbulence kinetic energy and dissipation rate profiles as input conditions. A major research gap in detailed computational fluid dynamics modeling is the uncertainty in the definition of these boundary conditions. The Joint Urban 2003 field study, which serves as the basis for this computational fluid dynamics study, provides ample measurements to base the initial and boundary conditions of the simulation. Several field cases have been identified as potential computational study cases based on an assessment of the meteorology and preliminary boundary conditions. Establishing boundary conditions for more data-sparse conditions will also be addressed.

The utility of computational fluid dynamics modeling comes from the fact that the equations of fluid motion are solved with an explicit incorporation of the important physical features. Therefore, a central input to an urban dispersion model is the urban geometry itself. A common format for describing urban geometry is the geographic information systems (GIS) shapefile format; however, computational fluid dynamics models often require CAD formatted files. As part of this project, a PNNL CAD expert developed a method for this conversion using the Oklahoma City building geometry set. Developing geometry files that have the characteristics necessary for computational fluid dynamics modeling (which include water-tight surfaces, and right-handed face orientation) is an area that will require more effort in the coming fiscal year.

To become acquainted with the STAR code, we conducted numerous test simulations in FY 2008. Simple geometry cases such as a single box within a small computational domain were explored to gauge model performance characteristics and to develop strategies for conducting the full city domain. Cases with simple geometries documented in literature were also examined to compare results from STAR with those from other codes. A portion of the Oklahoma City domain was also tested to assess the process of conducting simulations with real geometry. Importing the CAD file, cleaning up the geometry, meshing the computational volume, defining boundary conditions, and running basic flow simulations were accomplished.

The STAR code has been exercised to determine that it has the utility to explore city-scale atmospheric processes. In FY 2009, work will continue on developing the Oklahoma City file to improve the quality of the geometry for use with the computational fluid dynamics software. A full domain will be constructed to simulate one of the field cases. The results of this simulation will be examined and refined as necessary to gain an improved understanding of the flow field through the urban landscape and main processes that determine downwind concentrations of material released within urban street canyons.

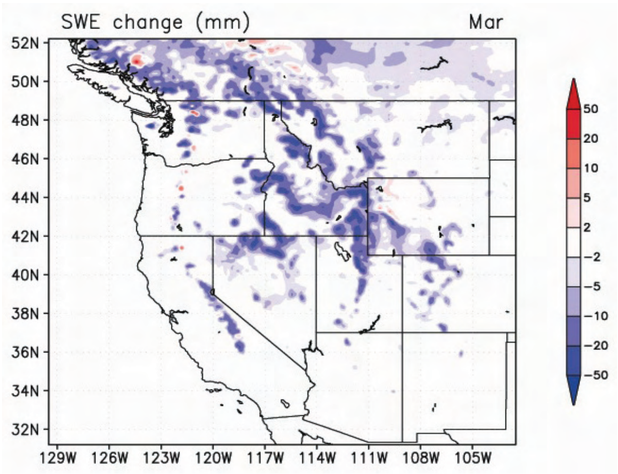
Effects of Soot Aerosol on Snow and Water Resources in the Western United States

Yun Qian, William I. Gustafson Jr., Lai-Yung Ruby Leung, Steven J. Ghan

◆ This project addresses an important problem linking environment (soot pollution) and energy (water resources) in the western United States. ◆

Soot is produced by the incomplete combustion of carbonaceous material, mainly fossil fuels and biomass. Black carbon is the main component of atmospheric soot particles. Soot from coastal cities in the western United States are transported inland by westerly winds and deposited on snow in inland mountain regions. This darkens the snow, reduces its albedo (i.e., the amount of energy reflected by snow into space) and causes the dirty snow to absorb more solar radiation than that of pristine snow. This indirect forcing of soot may accelerate snowmelt and alter stream flows, thereby contributing to a trend toward earlier melt dates in the western United States. The 2007 IPCC report listed the radiative forcing induced by "soot on snow" as one of the important anthropogenic forcings affecting climate change between 1750 and 2005.

Water resources in the western United States derive predominantly from cold season precipitation and storage in the snowpack. Mountain snowmelt accounts for more than 70% of the annual stream flows that support irrigation in the semi-arid Central Valley and Columbia Basin, hydropower generation, and navigation in the major river basins. Measurements show that snowpack has declined considerably throughout the western United States since the 1950s. Previous regional climate modeling and water resource studies in this region have focused mainly on the effects of greenhouse warming rather than aerosols. This study represents an attempt to investigate the aerosol effects of air pollution on water resources in the western states using an advanced regional aerosol-chemistry-climate modeling system that can simulate the deposition of soot aerosol and the impacts of soot-induced albedo perturbations on snowpack and stream flows.



Model results showing that soot-induced snow albedo perturbation cause a 10-50 mm decrease of snow water equivalent during March over mountain ranges in west America.

During FY 2006 and 2007, the ability to calculate different types of soot deposition as the model integrates forward in time was incorporated into the PNNL version of the Weather Research and Forecasting Model with Chemistry (WRF-Chem). A year-long simulation was performed using WRF-Chem to determine the soot deposition. The chemistry simulation shows large spatial variability in soot deposition that reflects the localized emissions and influence of the complex terrain. The snow albedo perturbations determined from the WRF-Chem simulation were then used to complete two 5-year-long WRF regional climate simulations, one with and one without soot-induced snow albedo reductions to investigate soot effects on the surface energy and water budget in the western United States.

During FY 2008, a third WRF-RCM simulation with doubled snow albedo perturbation was done to investigate the uncertainties and sensitivities of climatic responses to snow albedo perturbations. Our simulations show that the soot-induced snow albedo reductions increase the surface net solar radiation flux during late winter to early spring, increase the surface air temperature, and reduce the snow accumulation and spring snowmelt. These effects are stronger over the central Rockies and southern Alberta, where soot deposition and snowpack overlap the most. The indirect forcing of soot accelerates snowmelt and alters stream flows, including a trend toward earlier melt dates in the western United States.

The soot-induced albedo reduction initiates a positive feedback process whereby dirty snow absorbs more solar radiation, heating the surface and warming the air. This warming causes reduced snow depth and fraction, which further reduces the regional surface albedo for snow-covered regions. For a doubled snow albedo perturbation, the change to surface energy and temperature is approximately 50% to 80%; however, snowpack reduction is nonlinearly accelerated.

The results from this study have helped characterize the linkage between manmade pollutants and water resources in the western United States. Supported by this project, we submitted one journal paper to the *Journal of Geophysical Research* (in review) and two conference papers in FY 2008. A collaborated proposal titled "Black Carbon and the Regional Climate of California" was also recently submitted to the California Air Resources Board.

Efficient and Practical Simulation of Transport and Dispersion of Contaminants from Within the Marine Environment

Tarang P. Khangaonkar, Zhaoqing Yang

◆ Development of transport dispersion of contaminants technology and its application to Puget Sound supports national security missions in particular by supporting DOE's efforts to reduce global danger from weapons of mass destruction and improve emergency preparedness along the energy-shipping corridors of Puget Sound. ◆

Puget Sound offers several tempting targets for potential acts of bio- and eco-terrorism. Extending inland from the Pacific Ocean through the Strait of Juan de Fuca along the northern boundary with Canada, the Sound hosts several commercial and passenger vessel traffic routes which, along with the associated ports, have been identified as the most significant targets in the region. Once "the incident" (release of contaminants through the deployment of weapons of mass destruction [WMD]) occurs, human losses could be significantly reduced if the first responders and rescue workers have immediate access to information, including contaminant plume locations, trajectories, concentration isopleths, transport and dispersion projections, and predictions of shoreline impacts.

An operational model of Puget Sound with the ability to provide required information to first responders currently does not exist. In line with DOE's mission to reduce global danger from WMD and enhance emergency preparedness along energy-shipping corridors, this project focuses on developing rapid-response technology, with Puget Sound as the site selected for the research. The project objective is to develop a tool that will enable fast, high-resolution, accurate simulations of the transport and dispersion of contaminant plumes resulting from releases in the Puget Sound marine environment. This capability is based on three-dimensional hydrodynamic and fate-and-transport models.

During FY 2007, we built the three-dimensional hydrodynamic and transport model for Puget Sound using a state-of-the-art Finite Volume Coastal Ocean Model developed by the University of Massachusetts. The model domain covers the entire Puget Sound, Strait of Juan de Fuca, and San Juan Islands. The model was set up on a 36-processor cluster computer on a parallelized mode, and preliminary results demonstrate the model's ability to simulate the hydrodynamics (currents, tides, salinity, and river plumes) in high grid resolution that will drive the contaminant transport.

The focus areas of the project in FY 2008 were: 1) expansion of the model domain across the U.S.-Canadian border to include the Fraser River and Georgia Strait (the northern boundary of the model was extended to the Johnstone Strait of Canada), 2) model calibration and validation in Puget Sound and the Straits, and 3) simulation contaminant transport released in Puget Sound through the linkage to the GNOME model developed by National Oceanic and Atmospheric Administration (NOAA) Hazardous Material Response Division.

To accomplish the above objectives, substantial additional data were required, including bathymetrics, river inflows, tides, meteorological forcing, and oceanographic data (tides, currents, salinities, and temperatures) for model calibration and validation. We obtained additional bathymetric data in Georgia Strait and around Vancouver Island from the Institute of Ocean Sciences, Department of Fisheries and Oceans, Canada as well as tide information for the open boundary condition at the Johnstone Strait and river inflows for the Fraser River input.

Model calibration and validation for Puget Sound is challenging because there are no synoptic data available for model calibration. To achieve the model calibration goal, we obtained available calibration data for the sub-basins of Puget Sound from Straits (NOAA), Hood Canal (U.S. Geological Survey [USGS], Admiralty Inlet (Snohomish Public Utility District), Central Sound/Main Basin (King County), South Sound (Department of WA Ecology), and Whidbey Basin (NOAA, Skagit River System Cooperative, Snohomish County, Skagit Watershed Council, USGS, The Nature Conservancy, Tulalip Tribes). Six independent runs were conducted for the purpose of model calibration, corresponding to different time periods (varying from two weeks to several months) based on the data availability in each sub-basin of Puget Sound. The calibration process included refinement of the model grid, modification of the model geometry and bathymetry, adjustment of initial and boundary conditions, and fine tuning of model parameters such as background eddy viscosity, bottom roughness, and friction. Good model-data comparisons have been achieved in the model calibration runs for all the sub-basins under different tide, meteorology, and river forcing. In collaboration with the NOAA Hazardous Material Response Division, a linkage was developed that allows the use of the GNOME model to produce rapid simulations of transport of released contaminants.

With the completion of model expansion and calibration for Puget Sound and the Straits, the PNNL-Puget Sound model now is ready for conversion to "Operational Model" mode, running in a real-time mode with implementation of continuous real-time tides, river, and meteorological inputs for application in support of emergency response in Puget Sound.

The Aerosol Modeling Testbed

Jerome D. Fast, William I. Gustafson Jr., Elaine G. Chapman, Douglas J. Baxter

◆ This research will result in the development of an aerosol modeling testbed (AMT) that streamlines how new aerosol process modules are tested and evaluated over a wide range of spatial and temporal scales. ◆

The current paradigm in the aerosol modeling community is a haphazard approach in which new numerical treatments are evaluated with a small data set and implemented in regional and global models with limited information as to whether the new treatments are better or more computationally efficient than the older ones. Assessing the true performance of new numerical treatments for aerosol processes among several independent studies is virtually impossible because other important processes (e.g., emissions, meteorology, and chemistry) that affect particulate evolution are not the same. Nor are new aerosol treatments evaluated for a wide range of meteorological conditions that are included in climate predictions.

To address these issues, this project is developing an AMT, which provides a systematic and streamlined approach for testing and evaluating aerosol process modules for real-world conditions. The framework will enable aerosol modelers to test their hypotheses regarding the theoretical and numerical representation of various aerosol processes (e.g., nucleation, coagulation, gas-to-particle conversion, secondary organic aerosol formation, cloud-aerosol interactions, aerosol-radiation interactions, deposition) when all other processes are the same. No other organization is exploring the systematic evaluation methodology that the AMT uses. Over time, the AMT will document improved model performance that quantifies the increased skill of predicting aerosol mass, composition, size distribution, optical properties, and radiative forcing along with computational efficiency. This information is needed by the modeling community to know which treatments are most appropriate for climate models, ultimately reducing uncertainties in global and regional climate change predictions.

During FY 2008, our research consisted of four primary tasks: 1) increasing the modularity of the aerosol process within WRF-chem, 2) developing the AMT-based on a systematic evaluation methodology of test cases (called the analysis toolkit), 3) porting the AMT to multiple computational platforms, and 4) testing new aerosol treatments from other investigators within the AMT framework.

As part of the first task, the code-control software SVN was used to update the AMT version of the WRF-chem model to be compatible with the community version 3 released in June 2008. SVN is used to differentiate between external (those from the user-community) and internal (those related to the AMT) development activities. The modularity of the code has been enhanced to obtain a more fair comparison between the modal and sectional aerosol treatments. For FY 2008, this involved developing a consistent methodology of treating aerosol optical properties and cloud-aerosol interactions for both approaches. The new aerosol optical properties successfully demonstrated the concept of distributing improved techniques to other scientists through the AMT.

Under the second task, approximately 90 percent of the data for the first testbed case was assembled into the format adopted by the analysis toolkit. The first testbed case uses extensive meteorological, chemical, and particulate measurements made during the March 2006 MILAGRO field campaign in central Mexico. We built upon the generic software tools developed in FY 2007 that extracts WRF-chem output in a format consistent with the available types of measurements, including continuous time series from instrumentation at fixed surface sites and intermittent data from mobile aircraft and satellite instrumentation platforms. We now have tools for aircraft and surface types of measurements. A lidar simulator was created that extracts model output to mimic data obtained from vertically pointing aerosol lidars. Statistical and graphical programs were also added to the analysis toolkit. Based on Gnuplot freeware for platform compatibility, the graphical tools were designed to provide users quick-look plots.

Portability and scaling tests of the WRF-chem code were performed on EMSL's MPP2 and NW-ICE high-performance computer clusters as part of the third task. Asynchronous I/O greatly reduced the amount of time spent writing output files using hundreds of processors. Initial tests were performed on Chinook, MPP2's replacement cluster, and found to produce realistic results. A Computational Intensive Research proposal was written to request a large block of computer time on Chinook to run the AMT and permit scientists outside of PNNL to access the AMT.

In the last task, an external collaborator began using and testing the analysis toolkit as part of her research. We also used the AMT to isolate the reasons for differences in the modal and sectional aerosol models in WRF-chem, including those related to treatments for dry-deposition and aerosol water. Presentations were made at two scientific conferences and DOE's Atmospheric Sciences Program (ASP) annual meeting (including a presentation to the DOE ASP program manager) to inform the potential users of the AMT and generate interest from the aerosol community.

During FY 2009, we will create a beta version of the AMT to disseminate to a larger group of external users, enhance the additional modularity of the code, complete the software tools for the analysis toolkit, and begin developing a "cloudy-sky" testbed case. Planned enhancements to the analysis toolkit include adding a satellite simulator, adapting a radar simulator from another LDRD project, and finishing statistics and graphics for surface-based instrumentation. The content of the white paper will form the basis of a journal article describing the overall objectives of the AMT.

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 as a cause of major concerns, whether it is the impacts of floods, pests and disease, or drought is not well-understood. This research will explore the fundamental reasons why such change occurs frequently in natural resources and how we may respond to it. ◆

Climate impacts have received attention in the scientific literature both domestically and internationally. In addition, ecosystem and natural resource effects from climate variability and change are now being documented, and there is a growing literature on coping and adaptation measures being suggested or implemented around the world. These observations present serious challenges to the modeling frameworks used in integrated assessment. To be complete, the models will need to represent both the consequences of climate changes and the measures proposed to deal with those changes. The aims of this project are to develop both the analytical engine for impacts in the integrated assessment models and an analytical framework for extreme or sudden events. In this project, we are conducting data analysis, model development, and ultimately model testing and evaluation.

The primary activities during FY 2008 have been the creation and initial exercise of the post-processor as well as an intensive effort to understand better the four selected areas for exploring the potential for threshold behavior (ordered in increasing complexity in the nature of the interaction between weather and impact): heating and cooling degree days, heat wave mortality, pine bark beetle infestation, and agriculture.

Heating and Cooling Degree Days. Data developed for ongoing work on heat wave mortality show quite different penetration levels for air conditioning across the United States. As temperatures warm, it is reasonable to expect that areas of the country where air conditioning is not now common will experience increases in air conditioning installation. While they may have a rather smooth underlying trend, cooling degree day changes also show substantial annual variation. Air conditioning demand can take three forms—increased initial installation, higher capacity installations, and increased run times—all of which substantially affect peak-load demands. There is the increased possibility for more brownouts or outright system failures as capacity limits are reached.

Heat Wave Mortality. As demonstrated by the 1995 heat wave in Chicago and the European heat wave of 2003, heat waves can have large-scale impacts on mortality. Measures of heat wave intensity depend on temperature and humidity, thus requiring estimates of both. While it is expected that the amount of moisture in the atmosphere will rise, it is not clear that relative humidity would do the same, as this is a function of temperature and moisture content levels. Extreme heat index levels require high temperature and high humidity; thus, understanding the likelihood of major mortality events depends on a variety of community characteristics and change in temperature and humidity.

Pine Bark Beetles. One can see the impact of pine bark beetles in the west simply by looking at images from Google Earth, where the contrast between living and dead forests is evident. The consequences include increased risk of fire, damage to the timber industry, and the potential for a large-scale extension of the range of the beetle. While beetles are endemic over wide regions, real damage often occurs after large-scale eruptions that overwhelm the natural defenses of pine trees. Simulation of the beetle life cycle suggests that there is a range of temperatures consistent with univoltinism, temperatures below which result in average life cycles requiring more than a year, while temperatures above allow life cycles of less than a year. The larger concern has to be whether the range of the beetles will extend into the jack pine forests of northern Canada, which has the potential to turn a current sink for carbon into a significant source.

Agriculture. Two regimes of concern for agriculture (rain fed and irrigated) require quite different analysis to understand the potential for threshold behavior. Observed threshold behavior is the result of management decisions. The set of climatic conditions relevant to these decisions is complex, as is the set of economic conditions that condition the farmer’s decisions. Unlike the beetle problem, the farmer makes decisions bearing on the potential for abrupt change on a regular basis, which means that understanding the role of climate in agriculture requires a farm level economics tool of some complexity.

Considering the four impact areas and what additional climate information would enable better analysis, some common themes emerge. In order to understand the potential for threshold conditioned behavior to emerge, it is rarely sufficient to simply have climate information; one needs models that can reflect the role of climate in the arena of concern. However, it is also possible to suggest obvious areas where improvements in the capacity of the existing post-processer would be of use. Common to all of the four impact areas is the need for data with a finer time scale than monthly.

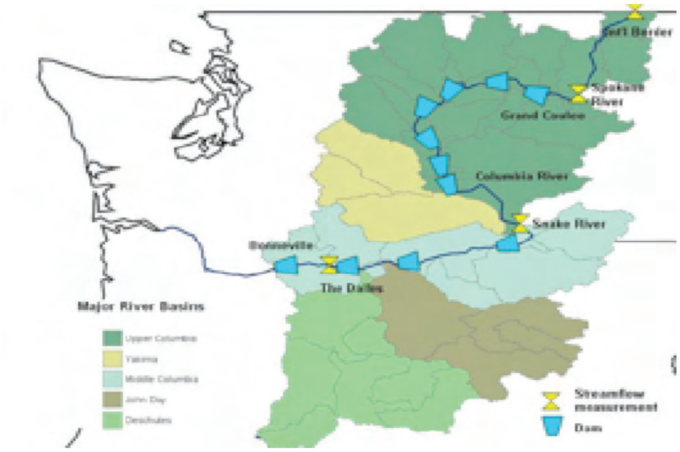
Energy Supply and Use

Bringing Water into an Integrated Assessment Framework

R. Cesar Izaurralde, Allison M. Thomson, Ronald D. Sands, Hugh M. Pitcher, Jacob Oppenheim

◆ We developed a modeling capability that can be applied to understand how water is allocated within a river basin and developed a system for modeling present and future water allocations among agriculture, energy production, and other human requirements as well as ecological needs. ◆

Water is an essential natural resource needed for food and fiber production, household and industrial uses, energy production, transportation, tourism and recreation, and natural ecosystem functioning. Anthropogenic climate change and population growth are anticipated to impose unprecedented pressure on water resources during this century. PNNL researchers have pioneered the development of integrated assessment models for energy and economic systems analysis under climate change conditions. This effort built a modeling capability to evaluate current and future water allocations between human requirements and ecosystem services.



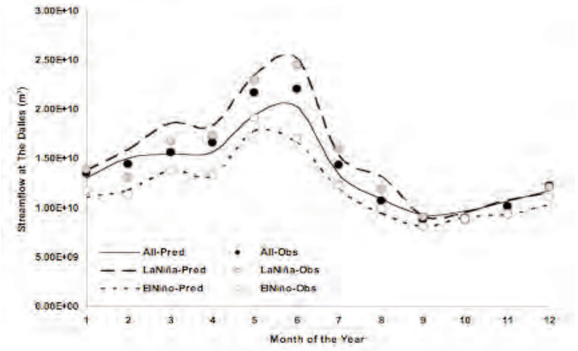
Map of the study basin, subbasins, and dams along the Columbia River.

The water prototype model (WPM) was built in STELLA® software, a computer modeling package that enables users to construct dynamic models to simulate and integrate biological, hydrological, economics, and sociological processes. The figure shows the 150,404 km^2 basin in the Pacific Northwest region that served as the platform for WPM development. About 60% of the basin lies in Washington, with the rest in Oregon. The Columbia River runs through the basin for 874 km, starting at the international border with Canada and ending (for the purpose of the simulation) at The Dalles Dam. Water enters the basin through precipitation, from streamflows originating from the Columbia River at the Canadian border and the Spokane and Snake rivers, and enters the Columbia River via runoff from land. Water leaves the basin through evapotranspiration, consumptive uses (irrigation, livestock, domestic, commercial, mining, industrial, and off-stream power generation), and streamflow through The Dalles. The model runs monthly to account for the impact of seasonal variations of climate, streamflows, and water uses. Data for the model prototype were obtained from national databases and ecosystem model results.

The WPM can be run from three sources: directly from STELLA, with the isee Player®, or using the web version of WPM constructed with NetSim®1 software. When running any of these three versions, the user is presented with a screen and a series of buttons, graphs, and a table. Two buttons provide the user with background on the model and instructions on how to run it. Currently, there are four scenarios that can be manipulated alone or in combination using the sliding input devices: interannual variability, climate change, salmon policy, future population, and biodiesel production. The model can also be used to simulate scenarios of climatic change alone or in combination with interannual climatic variability.

The WPM captured the effect of changes in streamflow conditions on hydropower production. Under La Niña conditions, more hydropower is available during all months of the year, with a substantially higher availability in the spring and summer months. Conversely, in El Niño conditions, hydropower will be less available, with a total decline of 15% from normal weather conditions over the year. In contrast, a policy of flow augmentation to facilitate the spring migration of smolts to the ocean would reduce the hydropower supply. Modeled hydropower generation was 23% greater than that reported in the 1995 U.S. Geological Survey database (81 TWh).

The modeling capability presented here contains the essential features to conduct basin-scale analyses of water allocation under current and future climates. Due to its underlying data structure and conceptual foundation, the WPM should be appropriate to conduct integrated assessment modeling at national and global scales.



Simulated and observed monthly streamflows at The Dalles under average, El Niño, and La Niña conditions, 1971-2000.

Carbonate Sorbents and Enzymatic Catalysts for Carbon Dioxide Capture

James R. Collett

◆ We are using carbonic anhydrase, an enzyme found in nearly all living organisms, to capture carbon dioxide from industrial, post-combustion flue gases. This approach shows great promise as a cost effective way of limiting greenhouse gas emissions from fossil fuel power plants. ◆

We are developing carbonic anhydrase as a catalyst for use with ammonia-based chemical sorbents for post-combustion CO_2 capture. This novel approach has potential to accelerate the kinetics of absorption and desorption of CO_2 by the solvent while 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/stripper hardware. Testing of the catalyst will be performed on a laboratory-scale, bench-top absorber/stripper system with the goal of continuously removing 90% of the CO_2 from simulated post-combustion flue gas streams.

We have tested the ability of carbonic anhydrase to catalyze the hydration of dissolved CO_2 in the presence of high ammonia concentrations such as those used in the chilled ammonia and aqueous ammonia processes for CO_2 gas removal from flue gas streams. Two continuously stirred tank reactors (CSTRs) containing 3.8 M at 13°C ammonia were placed side-by-side and sparged with 15% CO_2 and 85% N_2 flowing at 0.5 LPM. One solution (CA+) was amended with 77 mg of bovine carbonic anhydrase enzyme; the other (CA-) served as a control and did not receive any enzyme. Below 9.0, the drop in pH was much faster in CA+ than in CA-, indicating that the conversion of dissolved CO_2 to bicarbonate had been accelerated by carbonic anhydrase. The rapid pH drop 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.

A higher rate of CO_2 absorption induced by carbonic anhydrase was also reflected in the higher percentage of CO_2 that was removed from the offgas emanating from the CA+ solution in the early period of the CO_2 sparging cycles in the experiment described above. At t=5 (the 5-minute mark), 80% of the CO_2 gas flowing through the CA+ CSTR was retained in solution, where only about 34% of the CO_2 flowing through the CA- CSTR was retained. By t=25, the percentage of sparged CO_2 captured by CA+ CSTR declined to 0%, indicating that the CA+ solution had become saturated with CO_2. As expected, the saturation of the CA+ solution with CO_2 gas occurred at about the same time (t=20-24) as when the pH curve for the CA+ solution flattened at its lower limit ~8.2. At this point, the percentage of captured CO_2 from the CA- CSTR offgas had fallen to only 14%, indicating that its solution had not reached equilibrium in regard to absorbing dissolved CO_2 and still had unused CO_2 carrying capacity. Together, the pH slope and CO_2 offgas results indicate that adding carbonic anhydrase to concentrated ammonia solutions can increase the CO_2 hydration rate to bicarbonate significantly with a corresponding increase in the CO_2 gas absorption rate into the solvent. Our observation of the ability of carbonic anhydrase to catalyze the hydration of CO_2 to bicarbonate effectively in the presence of such high ammonia concentrations is a new and unexpected discovery. Kinetics studies of carbonic anhydrase of which we are aware typically have been conducted under conditions within the viable ranges of known living organisms. To our knowledge, no one has ever published or otherwise previously disclosed experiments that test the functionality of any form of carbonic anhydrase in the extremely high concentrations of ammonia that we recently tested.

In FY 2009, a computer-controlled system for continuous bench-scale CO_2 absorption and desorption tests will be assembled using CSTRs on a Sixfors fermenter rack system equipped with digital mass flow controllers and a customized LabVIEW program for process control and data acquisition. The system will be configured for automated, steady-state operation and data collection for up to several days or weeks at a time. Rich, lean solvent will be continuously circulated between the absorption and desorption CSTRs using peristaltic pumps that will also be digitally controlled via the LabVIEW program. Experience from the operation of this system will then be used to build and operate bench-scale packed columns that more closely resemble the kinds of absorber and stripper towers used at the plant scale for ammonia-based CO_2 capture.

Reaction kinetics data from the experiments above will be added to rated-based Aspen Plus process engineering models that simulate the unit operations of the aqueous ammonia process for post-combustion CO_2 removal from the flue gas of a 550 MW coal-fired power plant. The model will be used to evaluate the benefits and costs of adding carbonic anhydrase to ammonia-based solvents to accelerate the absorption and desorption of CO_2 at the plant scale. We will also investigate the genetic engineering of thermostable carbonic anhydrases to increase the operating temperature limits of the enzyme.

Deep Desulphurization of Hot-Coal Gas for Production of Liquid Fuels

Liyu Li, David L. King, Kake Zhu, Jun Liu

◆ An integrated total sulfur removal system consisting of a metal oxide-based sorbent plus a metal-based adsorbent will be able to remove sulfur in hot-coal gas to parts-per-billion (ppb) levels and prevent the downstream Fischer-Tropsch catalyst from being deactivated by sulfur poisoning. Such an integrated technology would be beneficial in both economic and technical terms when compared with the conventional wet-scrubbing desulphurization process. ◆

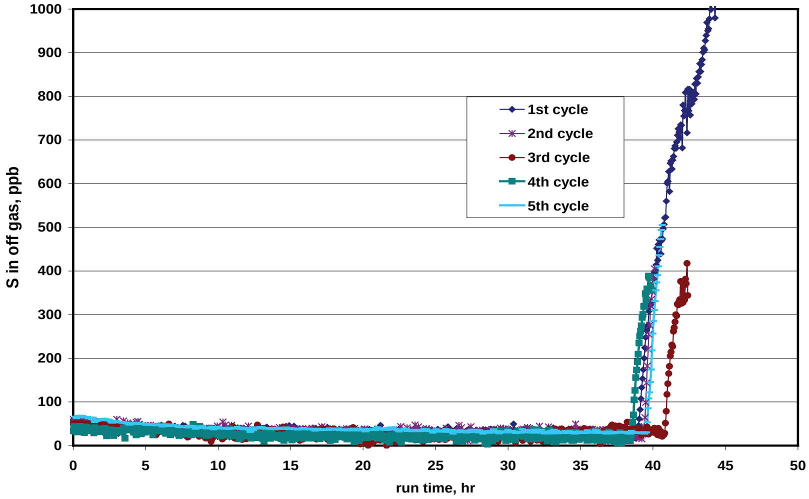
Gasification of coal or biomass to syngas followed by catalytic synthesis of liquid hydrocarbons or oxygenates provides a feasible strategy to meet the increasing demand for transportation fuels. A significant challenge is posed by sulfur present in the syngas, which poisons these catalysts even at low parts per million (ppm) levels. Although technical approaches exist for removal of these sulfur species to such low levels, they are rather costly and energy intensive, employing solvents at ambient or lower temperature and backup sacrificial adsorbents.

Since catalytic processes for the production of fuels and chemicals typically operate in the 225-300°C range, a process capable of removing sulfur gases to less than 50 ppb at or slightly above the temperature of the synthesis step is much preferred. Several warm syngas clean-up technologies have been recently developed based on metal oxide sorbents, primarily zinc oxide-containing materials. However, sulfur gases can be removed only over a regenerated zinc oxide absorbent to the few ppm level, which is insufficient for synthesis work. By trapping metal (nickel-copper alloy) nanoparticles in cubic mesostructured silica SBA-16, we have developed a class of regenerable adsorbents that efficiently captures low ppm level of sulfur from warm syngas. By means of chemisorption of sulfur-containing molecules on their surface, the metal nano-particles reduce the sulfur concentration to less than 50 ppb at 300°C.

Most of the reactions were carried out in a temperature-controlled fixed bed. Sulfur concentration and speciation were analyzed using our gas chromatograph-sulfur chemiluminescence unit that can detect sulfur concentrations as low as around 50 ppb in gas samples. A micro-gas chromatograph was used to monitor coal-gas composition changes before and after sulfur removal. Most of the characterization tests were carried out with our AMI-200R-HP reaction unit in Pittsburgh, PA that automatically controlled feeds to a temperature-controlled reactor. The gas-phase products from this unit were monitored with a gas chromatograph and an online mass spectrometer.

The three-dimensionally interconnected cage structure of the mesoporous support SBA-16 allows good accessibility of sulfur gases to the active sites and confines the metal particles within its nano-sized cages, which hinder metal particle migration and sintering under harsh conditions of desulfurization and regeneration. The sulfur-loaded adsorbents can be regenerated using a sequential oxidation-reduction process using air and dilute syngas. An integrated sorbent system comprising ZnO and confined metal nano-particles has been demonstrated that can regenerably remove sulfur in simulated warm biomass syngas down to less than 50 ppb with more than 10 wt% sulfur capacity. This solid adsorbent-based warm deep desulfurization approach can provide economic advantages compared with existing technologies.

In addition to providing a practical approach to sulfur deep removal from warm syngas, this work also provides new insights on the stability of nanoparticles within controlled mesostructures. Metal and metal oxide nanoparticles supported on high surface area materials are widely used in industry, but preventing particle agglomeration and sintering has remained a challenge. Our study suggests that the stability and activity of nanoparticles may be substantially enhanced by the judicious choice of the pore architecture that confines them.



Deep desulfurization of warm coal syngas using a metal-based sorbent. Feed gas: 18% H_2, 12% CO, 10% CO_2, 50% H_2O, 36 ppm H_2S, 6% CH_4, 4% He; flow rate: 12,000 hr^{-1} gas hourly space velocity; absorption temperature: 300°C; sulfur loading at 40 hrs is ~3.2 wt%.

Development of a Scaleable Water Resources Management System

Mark S. Wigmosta, Lance W. Vail, André Coleman, Kashif Gill

◆ This project developed and demonstrated next-generation tools to improve the operational efficiency of energy systems in the form of a scalable water resources management system that demonstrates tradeoffs between multiple energy-related water management objectives using improved snow and water forecasts. This system is expected to provide data critical to the more efficient operation of a constrained energy system. ◆

Managing energy and water resources requires looking for increased operational efficiency rather than wholesale changes to infrastructure. Improved methods for stream flow forecasting and new tools to access and manage uncertainty will enable resource managers to optimize operations. This project coupled next-generation hydrological and hydraulic simulation models with advanced remote-sensing and sensor technology to develop an operational tool to define more accurately the location, capacity, storage, and fluxes of water within a river basin. This operational tool uses advanced methods to generate ensembles of stream flow forecasts that can be used to manage water resources with explicit consideration of uncertainty in the climate forecasts. The ensemble forecasts are used with multi-objective optimization to yield a fully integrated dynamic system description with outputs for energy production, environmental constraints, flood control, recreation, and water supply.

During FY 2006, our activities demonstrated the feasibility of multiscale hydrologic simulations across the Columbia River Basin and the use of remote-sensing, time-series data to improve model performance and to characterize hydrologic controls on the dynamic water budget. These activities were a necessary first step for managing water and energy resources by developing the data infrastructure and analysis tools to understand the abundance and distribution of water resources. FY 2006 activities laid the groundwork for a scalable water resources management system that clearly articulates tradeoffs between multiple energy-related water management objectives using improved snow and water forecasts.

During FY 2007, we focused on development of a daily ensemble stream flow forecasting system using data assimilation of stream flow and spatial snowpack that considers the uncertainty in meteorological forecasts, model structure and parameters, and observations used for model updating. The model is run over a spatially distributed computational grid structured to align with the pixel resolution of various remote-sensing snow products.

The ensemble of model output generated using a meteorological ensemble and sampling from the feasible parameter space is combined with the ensemble of stream flow observations to update the model state using the Ensemble Kalman Filter, a data assimilation scheme. The model output ensemble is assimilated with the observation ensemble using a weighting scheme governed by the covariance of the model. As the observation error covariance approaches zero, the observations are trusted more; conversely, if the model estimate error covariance approaches zero, observations are given less and predictions more weight.

Our forecast system was applied to the Dworshak Reservoir in Idaho to evaluate daily short-range forecasts with observations and seasonal predictions against observations and National Resource Conservation Service (NRCS) April-July forecasts. The one- and three-day inflow forecasts for FY 2006-2007 showed agreement with observations. The ensemble spread bracketed the observations for the full time period with a slightly greater spread in the three-day forecasts.

Our April-July volumetric forecasts were found to be superior to NRCS forecasts in six of the eight years examined, providing usable information roughly six months earlier than the regression-based approach. Observations are generally well-bracketed within the 25th and 75th percentile bounds by the March 1 ensemble forecasts. The increased accuracy, longer lead times, and greater temporal resolution of our approach over traditional regression-based forecasts allowed use of advanced system optimization for improved energy-related water management.

During FY 2008, our research focused on the water and energy optimization theme. A multiple-objective ensemble optimization system was developed leveraging forecast technologies developed under this project and ongoing Laboratory work using machine learning and evolutionary computing. The optimization system was demonstrated for the Dworshak Reservoir, a multi-purpose reservoir with responsibilities for flood control, hydropower production, recreation, and fish and wildlife. Cold-water releases from Dworshak Reservoir have been used to moderate summer water temperatures in the lower Snake River since 1991. The optimization system was used to optimize power production while meeting recreation and flood control storage targets, and minimizing water temperature violations at the Lower Granite Reservoir. The optimization system was run for Water Year 2006 under a simplified set of operating rules and showed increased power production and a reduction of water temperature violations compared with historic operations.

Direct Coal Liquefaction

John C. Linehan, James A. Franz, Dean W. Matson, Mikhail S. Alnajjar

◆ This project investigated methods for the direct liquefaction of coal to feedstocks suitable for fuel and petrochemical processing in existing petroleum refineries. ◆

The U.S. and many other nations have large coal reserves which can be used for energy production and, with the current costs of petroleum based products, can be used for transportation fuels and chemicals. A research area curtailed in the 1990s was around direct liquefaction of coal to produce liquids capable of being upgraded using current petroleum-based refineries. With the current elevated price of oil on the international market, there is renewed interest in using non-petroleum sources for the development of liquid feedstocks suitable for fuels and petrochemical processing.

This project investigated methods for the direct liquefaction of coal to products suitable for processing in existing petroleum refineries. Experimental efforts focused on the development of inexpensive nanophase iron-based catalysts produced using a flow-through hydrothermal process. Catalyst testing was undertaken using model compounds, well characterized coals, to evaluate overall effectiveness and selectivity of the catalyst materials toward cleavage of specific bonds.

In FY 2007, we were able to build upon the Laboratory's coal liquefaction capabilities which included the production of catalyst precursors in multi-gram quantities, to synthesize nanophase iron-based catalysts in which the iron oxide was doped with nickel, molybdenum and cobalt at the 1, 5, and 10% levels. Initial work had shown that nano-iron catalysts were very good at hydrocracking and poor at hydrogenation. To produce feedstocks suitable for current petroleum refineries we need higher hydrogen-to-carbon (H:C) ratios than can be produced using iron catalysts alone. The advantage of our approach lies in that we can potentially tailor the H:C ratio of the coal liquids by adding small amounts (ppm to ppb) of an additional co-catalyst to the iron-based catalysts to promote hydrogenation and this could be accomplished without any extra added processing costs. The rapid thermal decomposition of solutes (RTDS) technique allows control of homogeneous metal doping of the iron-based catalysts.

The doped iron-oxides produced were found to be active carbon-carbon bond cleavage catalysts for naphthylbibenzylmethane (NBBM). However, the molybdenum and nickel doped iron-oxide catalysts were less effective in producing carbon-carbon bond cleavage products in reactions with the NBBM model compound than with the iron-oxide alone. The analysis of the doped materials showed that the bulk of the iron-oxide (if not all) was still in the same structural configuration as the iron-oxide by itself. The catalyst results may be due to the higher reaction rates for hydrogenation vs C-C bond cleavage evidenced for higher dopant loadings. Hydrogenation and C-C bond cleavage may be competing for the same reagents.

We also began initial studies of the catalytic hydrodeoxygenation (HDO) of the heteroatom containing moieties in coals. Preliminary results which demonstrated the successful conversion of 2-naphthol to naphthalene and tetrahydronapthalene at 400°C in a glass reaction tube suggested that the iron-based nano-catalysts developed under this project may be useful in converting coals into useful chemical feedstocks.

In FY 2008, our research included the continued development of new catalyst formulations still based on low-cost nano-iron particles produced using the RTDS method. Testing of the catalyst activity with the Argonne premium coal Wyodak in 10 ml tube unstirred reactors under hydrogen pressure at 400°C showed that moderate enhancement (1-7% increases in soluble products) of tetrahydrofuran (THF) solubles was observed with the iron-based catalysts. We were unable to observe the dramatic enhancement in THF solubles observed at Sandia National Lab with similar catalysts in a stirred reactor. Design and production of a sonication reactor to enhance mixing was accomplished. Heat-up times in the sonication reactors were much faster than for strictly thermally heated reactors.

In a detailed study with and without coals we were able to demonstrate that these inexpensive iron-based catalysts were indeed effective HDO catalysts. Naphthol was reproducibly converted to naphthalene and tetralin in high yields. We also demonstrated that coal inhibits the HDO process during coal plus naphthol experiments. This inhibition may again be due to competing reactions with the HDO catalysis. However the poisoning of the HDO catalysts by some reagent in the coal cannot be ruled out. We developed an analytical technique for the quantitative analysis of naphthol and its products. We obtained the first completely anaerobic powder X-ray diffraction analysis of the catalyst used in a direct coal liquefaction reaction. The material characterization unequivocally established that the ferrihydrite precursor was completely converted to $Fe_{.97}S$ under reaction conditions.

This research has further expanded PNNL's capabilities in the area of production of nanoscale catalysts for coal liquefaction in which high activity iron-based environmentally benign catalysts were synthesized and tested on coals and coal model compounds. The catalysts produced under this project were independently tested and found superior to all other iron-based coal liquefaction catalysts.

Electrolyte Development for Next Generation of Lithium Ion Batteries

Jason Zhang, Wu Xu

◆ Hybrid electric vehicles (HEVs) and plug-in hybrid vehicles (PHEVs) need to have a battery that can store more energy per unit volume and weight than the state-of-the-art lithium (Li) ion batteries. These batteries also need to undergo many thousands of charge-discharge cycles. The two ways to augment each cell's energy storage capacity significantly include increasing voltage by using high-voltage cathode materials, and increasing the amount of charge stored reversibly per unit weight and volume of the cell normally by using other anode materials such as silicon (Si). Both methods require new electrochemically stable electrolytes, the development of which will enable the use of high-voltage cathodes and the success of Si as anode materials for the next generation of Li ion batteries. ◆

Existing Li ion battery technologies have several drawbacks including limited energy storage capacity, high cost, limited cycle life, and some safety concerns, especially above 4.3 V. To increase significantly both the energy density of the batteries or the amount of charge stored reversibly per unit weight and volume of batteries, one can use high-voltage cathode and/or high-energy anode materials such as Si. However, enhanced battery capacity in high-voltage cathode materials is accessible only at potentials close to or over the oxidation of presently available electrolytes, which 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, which cause disconnection of active particles and thus a sudden, sharp decreased capacity 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.

This project started in mid-July 2008. A through literature search identified several potential salts and solvents that are good candidates for the required applications. Most key materials were ordered, including fluorinated carbonate solvents (monofluoroethylene carbonate and trifluoropropylene carbonate) for high-voltage cathode applications. Several electrolyte additives are used in Li ion battery electrolytes, high-voltage cathodes, and low-voltage anode materials. A hood with required hardware has been set up for chemical synthesis.

Our efforts focused on enhancing the stability of the Si-based anode. The effect of electrolyte components on the performance of Si anode materials was investigated. The Si electrodes were prepared by mixing 80% Si powder as active material, 12% conductive carbon black, and 8% PVDF as binder. NMP was used as the solvent to dissolve PVDF binder. The well mixed slurry was cast on a 25 μm thick Cu foil. After the solvent was evaporated, the sample was compressed and dried in a vacuum. Two Si powders from different suppliers were used to cast Si anode samples. The effect of sodium (Na^+) and potassium ion (K^+) additives in electrolytes on the cycling stability of Si anode have been investigated. CR2325 type coin cells were assembled with a Si electrode disc (ϕ 5/8 in) as cathode, an Li disc (ϕ 5/8 in and 0.75 mm thick) as anode (Aldrich), two layers of Celgard 2501 polypropylene separator, and three different electrolytes (1 M $LiPF_6$ in EC/EMC as control and also with 2% $NaPF_6$ and KPF_6 as additives). The assembled cells were cycled between the voltage range of 0.02-1.20 V versus Li^+/Li.

The results of electrochemical testing data reveal that the addition of 2% $NaPF_6$ in the control electrolyte leads to a lower capacity of Si-based electrode, while the addition of 2% KPF_6 in the control electrolyte improves the capacity of the Si electrode, which will be further investigated in FY 2009. The effect of the size of Si powders, carbon coating, and salts and solvents on the performance of the Si-based anode will also be further investigated.

High-voltage stable electrolytes will be investigated in FY 2009. Several commercially available fluorinated cyclic carbonates will be tested with a high-voltage $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/graphite battery system. The fluorinated linear carbonates such as bis (2,2,2-trifluoroethyl) carbonate will be synthesized in this work. Electrolytes with the appropriate Li salt and solvents compositions will be formulated to achieve improved electrochemical and thermal stability at voltages above 4.3. An additive will be selected to improve electrolyte safety.

The success of this project will lead to an electrolyte that is stable at more than 4.3 V, which is critical for the application of a high-voltage electrode and whose combination can increase the energy density of the Li ion battery by 20-40%. It will also lead to an electrolyte that can enhance cycle life of the Si-based anode. These electrolytes will enable a practical application of a novel cathode and anode and significantly improve energy density and the safety of Li ion batteries used for HEV and PHEV applications.

Human Factors for Situational Awareness in Power Grid Operations

Ross T. Guttromson, Jeffery E. Dagle, Frank L. Greitzer

◆ Training for electric power grid operators typically employs simulations that are limited to the footprint of an operator's own area of expertise; it rarely provides experiences with distributed systems and associated operationally relevant critical decision-making and communication skills. This research defined and demonstrated the use of cognitive science-based training management concepts that advance the state of practice for training of complex decision-making tasks. ◆

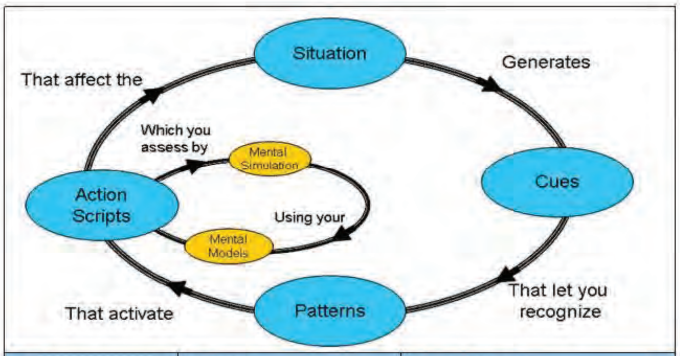
During the actual operation of the power grid, operators' actions influence and are influenced by other nearby systems and balancing authorities. When applied to wide-area power grid operations, our training method offers new and more detailed criteria for identifying deficiencies in critical decision making and situation awareness of operators and teams engaged in realistic, simulated wide-area power grid operations. This management approach promises to accelerate and improve the effectiveness of electric power grid operational training and extend the operational.

The purpose of this research was to apply advanced theory and models of naturalistic decision making within a cognitive engineering framework to develop new task and performance analysis criteria that may be employed within a realistic electric power grid simulation environment to enable more effective training management and human factors testing and evaluation of operational displays and procedures. This project addressed the lack of grid situational awareness leads to sub-optimal decisions and the failure to communicate adequately and share critical status information with other balancing authorities and reliability coordinators contributing to poor situational awareness. We defined grid operator training methods within a sense making and situational aware perspective that applies cognitive engineering and naturalistic decision-making models to guide training management and mitigation decisions.

Situation Awareness Framework. We applied Klein's naturalistic decision-making model, the Recognition-Primed Decision Model (RPDM), which describes how experts make decisions. The decision maker extracts cues from the situation that enable him or her to recognize patterns or learned relationships among cues that may be associated with solutions or action scripts. The decision maker then tests action scripts by running mental simulations within mental models that reflect the operator's situational aware. Our research extended the RPDM to power grid operations at a level of detail sufficient to define specific training mitigation strategies.

Improved Situational Awareness Training Management. The RPDM model was applied to a restoration training scenario developed for the simulated operational environment to demonstrate the training approach and highlight the efficacy of the EIOC for training situational awareness and communications for shared awareness. Specifically, we defined cues, patterns, and mental models that apply to power restoration scenario from which we developed learning objectives that are directly tied to required knowledge (i.e., enabling and terminal learning objectives). These serve as criteria for training intervention strategies to identify and mitigate performance that falls below instructional objectives. Cues, patterns, and a collection of 17 mental models were defined. The application of this cognitive learning framework was described in a live, distributed wide-area training capability demonstration. The RPDM process is illustrated below, along with an example of a cue, a pattern, and a mental model relevant to the operational scenario developed for demonstration purposes.

We applied and articulated a framework for using naturalistic decision-making models in power grid human factor studies and training. The research demonstrated how to create more detailed, prescriptive training mitigation strategies that advance the practice of electric power grid training, and how these capabilities could be applied to operationally relevant power grid training and human factor/situational awareness assessments of proposed controls and displays.



Cue	Pattern	Mental Model
MVAR reserves in an area	System on verge of voltage collapse	Adding capacitance will increase local bus voltages

RPDM and examples of relevant cues, patterns, and mental models.

Investigation of Exfoliated Graphite Oxide as a Potential Supercapacitor Electrode Material

K. Scott Weil, Jin Yong Kim, Jeff F. Bonnett, Jung Pyung Choi

◆ Energy storage technologies are vital to future global clean-energy development or renewable energy sources. Effective methods of storing energy (particularly electrical) will ensure that a continuous supply can be maintained from a more distributed and intermittent source base (e.g., solar, wind, or tidal) for stationary and transportation applications. ◆

Conventional batteries store more energy than capacitors but discharge at a much lower rate; thus, they exhibit low power densities. Traditional capacitors can provide a burst of power but do not store much energy. Also known as ultracapacitors or electrochemical capacitors, supercapacitors employ high-surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. By doing so, they attain greater energy densities than conventional capacitors while possessing the same high power density characteristics. These energy storage devices are being considered for a variety of uses, including new hybrid and light duty electric vehicle designs to improve vehicle efficiency via engine/battery downsizing and by recapturing energy during braking. Because of their rapid discharge ability, supercapacitors offer a straightforward way to handle peak loads (e.g., during vehicle acceleration or hill climbing).

The amount of charge that can be stored in a carbon-based supercapacitor generally depends strongly on the amount of solid surface that can be accessed by the electrolyte (and thereby set up the ionic double layer in which charge is stored). For example, while activated carbon is ubiquitously employed in a number of electric double layer supercapacitor designs from its low cost and high surface area, its specific capacitance in practice is somewhat limited because a large fraction of the material surface area in this material is in pores that cannot be accessed by ions in the electrolyte and thus is essentially inactive. This is particularly problematic for the higher capacitance organic electrolytes in which ion size is much larger than aqueous electrolyte ions.

Comparative capacitances of four activated carbons (currently employed in commercial supercapacitors) and PNNL-synthesized grapheme.

Carbon Powder Type	Relative Discharge Capacitance
Norit DARCO KB-G	1
Norit DARCO KB-WJ	1.16
Sanwa RP-20	4.26
Sanwa YP-17D	6.25
Pure Graphene	44.02

Exfoliated graphite (or graphene) was anticipated to maximize the useable surface of the carbon relative to activated carbon and thereby lead to a substantial increase in capacity. In this project, we developed a facile chemical route to synthesize high quality graphene in large-scale quantities (0.1 kg or more per batch, with the potential for larger quantities) as well as the ability to produce surface functionalized versions of it via the reduction of graphite oxide with various organic reagents. In addition, various team members conducted preliminary tests on pure graphene to assess its potential use in electrical energy storage applications, finding that: 1) the addition of a small percentage of graphene can vastly improve the specific capacity of metal oxide-based Li-ion batteries (i.e., storage capability), particularly at high charge/discharge rates, and 2) pure graphene offers nearly an order-of-magnitude improvement in capacitance—i.e., electrical charge storage capability—relative to baseline commercially purchased activated carbon materials (designed and sold specifically for the supercapacitor market).

Our current synthesis process consists of forming exfoliated graphite oxide and partially or fully reducing this material to form functionalized or pure graphene. X-ray diffraction and transmission electron microscopy analyses demonstrated that single sheet graphene could be formed under the above processing scheme. FTIR analysis demonstrates via tracking of the C=O stretching vibration (at 1750 cm^{-1}) in the graphite oxide precursor that while reduction can be carried out partially or in full, the former allows the possibility of producing functionalized graphene (i.e., a material that can be modified in numerous ways by chemically tailoring the oxygenated functional group). Subsequent electrochemical testing indicated nearly an order-of-magnitude increase in capacitance in pure graphene relative to a series of high quality used activated carbons employed in commercial supercapacitors, as shown in the table below. In addition, a form of the material was prepared that incorporated a nanoscale oxide particulate bonded to the base graphene sheet via the oxygenated functional groups (i.e., formed from partially reduced graphite oxide). Due to the pseudofaradaic nature of the oxide, this composite material is expected to show an even greater enhancement in storage capacity. In addition, it is speculated that analogous composites (prepared using alternative oxide compounds) may offer interesting catalytic properties.

Liquid Carbon Dioxide Coal Slurry Research

Robert J. Robertus, Michael G. Dodson

◆ Current coal gasification projects are capital intensive, expensive to operate, and not as reliable as coal combustion furnaces. Successful development of a carbon dioxide-coal slurry pump/delivery system will reduce capital costs, improve reliability, and increase the efficiency of coal gasification plants. ◆

Coal gasification projects use either pre-dried coal and lock hopper feed systems or water-coal slurry to feed the high-pressure gasification systems. Both methods reduce the operating efficiency of the coal gasification plants. As the nation moves to CO_2 sequestration, waste liquid CO_2 may be used to form CO_2 coal slurry to feed high-pressure gasifiers at a lower cost per kilowatt of output. Successful development of a coal-CO_2 slurry pump/delivery system will reduce capital costs, improve reliability, and increase plant efficiency, the former two of which are critical needs for coal gasification in the United States.

Current gasifier technology is divided into two camps: water slurry and dry coal feed. Water slurry feeds can be concentrated to only 53 to 66 wt% dry coal, depending on the coal's inherent moisture content. The excess water is evaporated at high temperature (2600ºF) and high pressure (1000 psia). Thermodynamically, this is a heavy energy penalty that lowers the cold-gas efficiency of the unit. Dry-feed systems must expend energy outside the gasifier to reduce the coal moisture content to 2% to ensure proper feed characteristics. We know this consumes substantial energy, and the moisture from the coal is not recovered. We also learned that liquid CO_2-coal slurry loadings of up to 88% dry coal have been successfully pumped in other applications. Because of the lower fluid content in CO_2 slurries (12-20% CO_2, 34-47% water), there is less to evaporate than with water. Further, the heat of vaporization for liquid CO_2 is only ~25% that of water. These two conditions can increase the efficiency of a low-rank coal gasifier by ~15%.

The aim of this project is to develop a feed system that can reliably deliver concentrated CO_2-coal slurry to a coal gasifier at pressures up to 500 psia for basic research and to feed the engineering-scale entrained-bed coal gasifier system at pressures to 250 psia continuously for long-term runs. This project was developed in three basic phases. Completed in FY 2006, the first phase included collecting CO_2 use data as a fluidizing medium for coal slurries. During Phase II, we designed and performed experiments that extended existing test data to operating temperature and pressure conditions predicted for the current and next-generation gasification systems. Phase III applied technologies from Phase II to supply CO_2-slurried coal to the experimental gasifier project.

During FY 2007, we analyzed gasifier technologies using the Aspen Plus simulator and showed that liquid CO_2-coal slurry-based systems reduced oxygen consumption in the gasifier while simultaneously increasing its cold-gas efficiency for a wide variety of coal and gasifier combinations. Our main accomplishment was the construction of a test loop for evaluating flow characteristics of CO_2-coal slurries in varying concentrations. We designed the test loop to withstand 4000 psia pressures at room temperature (maximum output of the pump) to be operated continuously for extended periods by adjusting valves around two stirred pressure vessels. Testing system integrity and operability at pressures under 15 psig, we successfully tested the flow system using pure liquid CO_2 to ensure that all fittings were leak-tight. We completed two tests with dilute slurries (7% coal in CO_2 and 50% coal in CO_2). The 7% test was quite successful, but the 50% test failed when the pump stopped.

During FY 2008, we fixed the damaged pump, added an accumulator to smooth the flow, and ran experiments with 0%, 30%, and 60% by weight of coal in liquid CO_2. The pump was able to stop and start at will when the system was under pressure at all coal loadings. The 60 wt % slurry was pumped for a sufficiently long period of time to heat the recirculating fluid from the compression energy of the pump. This caused predictable changes in flow and density. The conclusion from the work was that the pumping system was be able to deliver at least a 60 wt% coal slurry to the PNNL gasifier.

Ready to operate the coal/CO_2 slurry test loop.

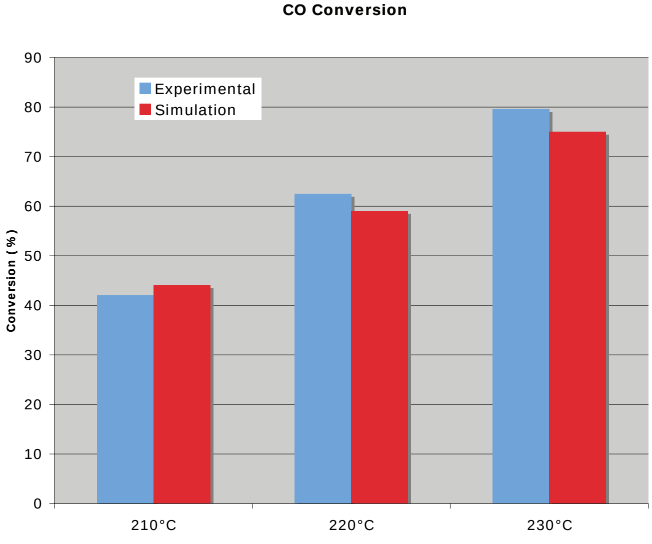
Liquid Fuel Synthesis Modeling

David R. Rector, Mark L. Stewart

◆ The hydrocarbon species distribution resulting from the Fischer-Tropsch process depends on the transport of reactants and products in the reactor. New reactor designs based on monolith geometries have been developed to optimize product distribution. Simulation capabilities to model the flow, transport, and reaction behavior in the reactor will lead to a better theoretical understanding and development of new reactor concepts. ◆

The syngas created by coal gasification is converted to a hydrocarbon fuel through catalyzed chemical synthesis such as the Fischer-Tropsch process, a surface catalyzed polymerization process that uses CHx intermediates formed by the hydrogenation of adsorbed carbon monoxide (CO) to produce hydrocarbons with a broad range of chain length and functionality. The Fischer-Tropsch reaction takes place in a three-phase system. The gas components consisting of CO, hydrogen, steam, and light hydrocarbon products pass through the liquid hydrocarbon product to the porous catalyst and react to initiate and increase the hydrocarbon chain lengths.

The goal of this research is to develop a simulation capability to optimize the resulting chain-length distribution and minimize processing required to obtain a useful final product. Process optimization involves maximizing the fraction of most desirable components that are in the middle distillate range (C_5-C_{20}). Base product chain length distribution is described by the Anderson-Schultz-Flory (ASF) theory, where the product yield decreases exponentially with chain length. The rate of reactant arrival and product removal from catalytic sites controls the local concentrations. Diffusion-limited CO leads to high H_2/CO ratios, decreasing C_{5+} synthesis rate and selectivity. Diffusion-limited removal of reaction products increases their role in secondary reactions; it can lead either to olefin readsorption and chain initiation, reactions that increase product molecular weight, or to olefin cracking or hydrogenation, which leads to lighter products. Control of mass transfer rates results in the tailoring of product distribution.



Comparison of simulation results with data for CO conversion in a monolith FT reactor.

Several different reactor designs have been developed over the years, including multi-tubular fixed-bed reactors, fluidized or ebullient reactors and most recently, slurry three-phase catalytic reactors. The first reactor design modeled in this project is a new ceramic monolith reactor concept being developed at PNNL. Monoliths are ceramic blocks of parallel, straight channels, the walls of which are coated with a thin layer of porous catalytic material that may range from 5 to 50 microns in thickness. The straight, open structure results in low pressure drop, and the small channel cross-section results in small diffusion lengths. A thin liquid layer is formed through which gas components diffuse to the surface. Once reactants reach the porous catalyst surface, they must diffuse into the layer to react, and products must diffuse out to be removed.

During the first year of this project, we developed simulation methods to describe the transport processes occurring in an Fischer-Tropsch reactor at the device scale and discrete liquid film/gas interface. A three-dimensional computational fluid dynamics simulation program was developed to model the monolith reactor. Each channel is subdivided into axial nodes, each of which contains four regions: syngas flow, liquid film, liquid in the catalyst pores, and catalyst surface. Each fluid region has a detailed chemical species distribution that includes syngas components, olefin and paraffin distributions, and water. The catalyst surface has a distribution of hydrocarbon chains. Equations are solved for liquid film flow, gas flow, species transport, and energy. The diffusion mass transport is driven by chemical potential differences calculated using the Peng-Robinson equation of state for mixtures.

During FY 2008, the simulation method was validated by comparing results with CO conversion data taken from a monolith Fischer-Tropsch reactor for a range of operating temperatures. The simulations showed that film concentration changes as a function of location in the reactor with a higher concentration of long chain molecules near the top of the reactor. A model was also developed for a conceptual porous wall monolith reactor to assess its performance.

Nano-Ribbon Membranes for Viable CO_2 Separation

Rick E. Williford (PNNL), Henk Verweij (Ohio State U)

◆ Coal-fired plants will continue to produce electricity for many years, so there is a need for inexpensive and efficient CO_2 separation technology for this and 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% CO_2 capture with <10% increase in energy cost by 2012. We consider flue gas as a mixture of CO_2 and N_2 and take effects of H_2O into account. Membrane separation has a principal advantage in that it can occur without external energy input, requiring no additional energy that would translate into operational costs. Because of the harsh operating conditions, materials to accomplish the above goals do not presently exist. A key feature is that the proposed ceramic membrane is stable and long-lived in flue gas environments, thus minimizing down time 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 permanence (throughput) and thus reduces efficiency important in industrial applications. The organic coatings are generally destroyed by the harsh chemical and thermal conditions in exhaust gases.

The technical objective of this project is 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 permanence of above 10^{-5} mole/m^2/Pa/sec, meeting the DOE goals. This scope encompasses 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 separative 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 the surface with CO_2 and excluding N_2. High permanence is achieved by using a very thin active membrane on a very porous support, the latter for structural integrity. The membrane is being developed using a technically diversified approach. One team is pursuing a nano-ribbon concept where the pores of the ceramic membrane are filled with a ceramic precursor, which then shrinks during calcination to leave 1 nm-wide ribbon-like pores along the original pore walls. The second team is using another technique to coat the pore walls, thus reducing pore diameter to ~1 nm. Both teams are using the same materials to achieve the same surface chemistries.

Both teams made significant progress in FY 2008. The nano-ribbon team 1) developed the chemistries for applying the pore fillers, 2) developed the dip coating and calcination processes to create the nano-ribbon pores, 3) produced structurally robust membrane assemblies, 4) obtained preliminary results verifying separations more than 30% higher than Knudsen transport mechanisms, and 5) demonstrated high permanence of ~10^{-5} mole/m^2/Pa/sec. The ribbon team is presently focused on eliminating the membrane defects that have kept the separability above 10 to date. The pore-filling team has 1) developed the chemistries for coating the pore walls, 2) developed spin coating and calcination processes for producing membranes with coated pore walls, and 3) solved their defect problems. Their focus is presently on experiments to demonstrate achievement of separability and permanence goals.

During FY 2008, our work indicated that a positive outcome can 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. The 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 will greatly advance DOE's agenda for carbon sequestration. The most important result was demonstration that the combination of small pore diameter and specific pore wall chemistry, which works to provide the CO_2/N_2 separation and CO_2 permanence that will ultimately be needed for industrial applications.

In FY 2009, the primary goals are to complete quantitative measurements of high separation and permanence of the two ceramic membrane designs and to begin positioning the project for scale-up to industrial applications. This includes collecting data to quantify the sorption and mobility of the gases on the pore walls and using this data to develop a model of the process. The model will then be used as technical support for an invention report in FY 2009 and for optimizing the separation, permanence, strength, cost, and lifetime of the membranes in FY 2010. Other candidate ceramic pore coating materials will be explored in FY 2009, thus demonstrating the wide applicability of this concept for separation of CO_2 from flue gases.

Power Systems Computational Advancements

Zhenyu Huang, Jarek Nieplocha

◆ This project intends to transform the power systems computational paradigm by increasing computational speed and improving grid operation functionalities to achieve adequate power grid situational awareness and better real-time grid control to avoid or mitigate power system blackouts. ◆

Modern power grids are inherently complex; high energy is moved between vast numbers of interacting components across thousands of miles. Harnessing the complexity to execute planning and operational tasks requires power system engineers to rely on computational capabilities and results for system security evaluation, system reinforcement, and design of remedial and preventive controls. Faced with new challenges from ever-increasing load demands and the market environment, power system computation is more important than ever for understanding power grid behaviors and managing the power grid operation.

This project aims to revolutionize power system computational processes. The technical advancements of this project are two-fold: 1) to improve the computational efficiency of traditional Supervisory Control and Data Acquisition (SCADA) measurement based grid operation functions (i.e., parallelized state estimation, parallel contingency analysis, and real-time market operation), and 2) to develop new grid operation functions driven by phasor measurement (i.e., phasor-based state estimation, dynamic state estimation, and look-ahead dynamic simulation). The essential technical barrier to today's real-time power grid control is the need to increase vastly the speed of state estimation, the procedure used to estimate power grid states from measured inputs of SCADA systems. State estimation is at the core of other power system operation functions, including contingency analysis, automatic generation control, and economic dispatch. The speed at which state estimation and contingency analysis are conducted (approximately every 5 minutes, typically) needs to be increased dramatically so that the analysis of contingencies is both comprehensive and can be conducted in real time. Furthermore, traditional state estimation is based on a power flow model and can provide a static snapshot of current system operation status but offers only a partial picture of situational awareness.

To complete the picture, we propose the concept of dynamic state estimation to include dynamics in the analysis and predict future system status based on the newly emerging phasor measurement technology. The dynamic state estimation enables dynamic contingency analysis and look-ahead dynamic simulation. All these new functions form a foundation for the next-generation power grid operation platform.

During FY 2006, phasor-measurement-based state estimation was developed to provide a high-level, wide-area, real-time view of power grid status. To estimate power system states from limited phasor measurements, we developed a novel method that combined the concepts of power flow solution and observable islands to formulate a hybrid power flow model. Also in FY 2006, we parallelized the Conjugate Gradient method for the weighted least square problem, which is core to static state estimation. The parallelized conjugate gradient method outperforms the state-of-the-art parallel linear solver techniques. Based on this parallelized Conjugate Gradient method, a parallelized state estimation software package was developed that achieved a first-ever 10-time speedup on 16 Cray MTA-2 processors for the western U.S. power system compared with a serial version.

In FY 2007, efforts continued on the development of parallel state estimation, parallel contingency analysis, and dynamic state estimation. Further improvement on matrix pre-conditioning achieved another 5 to 10 times improvement in state estimation efficiency, showing the potential to achieve a state estimation process time comparable with the SCADA measurement cycle. Parallel contingency analysis, which studies "what-if" situations, was developed with dynamic computational load balancing. Tests of the parallel "N-1" contingency analysis using the western U.S. power system model achieved a speedup of 26 times on a 32-processor cluster computer, indicating a fairly linear scalability. The problem of dynamic state estimation was formulated as a two-step process – "prediction" and "correction" – using the Extended Kalman Filter technique.

During FY 2008, we continued our efforts on massive parallel contingency analysis, dynamic state estimation, look-ahead dynamic simulation, and real-time market operations. The parallel contingency analysis framework was further improved to conduct "N-x" contingency analysis. Massive "N-2" and "N-3" analysis achieved about 470 times speedup on 512 processors. To maximize the computational performance, the dynamic load balancing scheme was improved by using multiple task counters and task stealing strategy so that computational load on individual processors was balanced to the maximum degree.

Based on the dynamic state estimation formulation developed in FY 2007, dynamic state estimation was implemented and tested with small- to medium-size systems. GlobalArray programming techniques were introduced to parallelize the computation of dynamic state estimation. The testing results led to some important conclusions: the dynamic state estimation based on the Extended Kalman Filter technique can successfully estimate system dynamic states; the developed method has very robust performance with respect to measurement noise, model error, and measurement sparsity; and most importantly, the developed dynamic state estimation concept is feasible with phasor measurements.

Power grid dynamic simulation consists of two major parts: numerical integration of differential equations and matrix manipulation for algebraic equations. The latter is ~80% of the computational load. We applied OpenMP to parallelize the dynamic simulation process. On a 1000-bus medium-size system, the parallelized dynamic simulation achieves 20 times speedup, which establishes a 5-minute look-ahead capability. The larger the system, the more speedup that can be achieved, and the further ahead we can look.

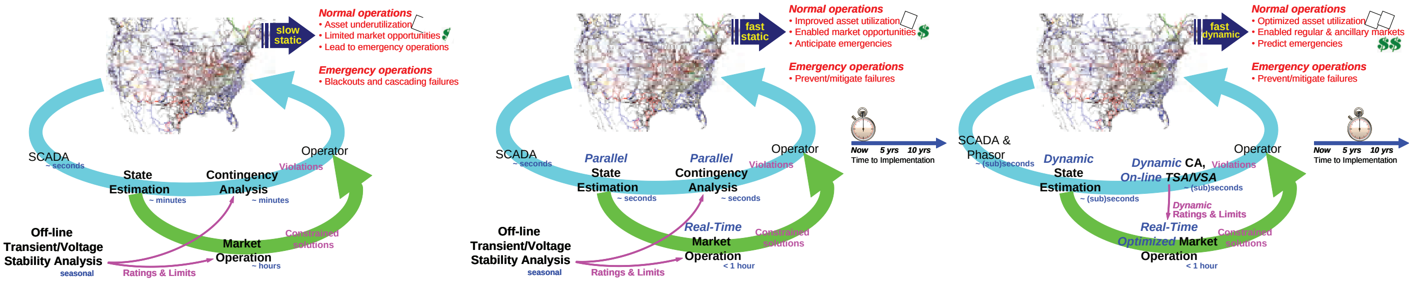
On real-time market operation, the central technique is optimization. Some of the market functions include unit commitment, financial transmission rights (FTR), and market performance monitoring. A new FTR formulation was developed for better computational efficiency. Proof-of-concept examples have been developed, demonstrating the validity of the formulation. This technology will increase the speed of FTR clearing and enable more comprehensive FTR categories. In addition, it is ready to be tested on real-market operations models.

Computationally, this project addressed many aspects of power system computation issues. We categorized time-domain power system computational algorithms into three groups: algorithms for well-determined equations, optimization algorithms for over-determined problems, and numerical integration algorithms for dynamic equations. Almost all the traditional power system algorithms are designed for single-processor computational environments. For decades, power engineers have evolutionally enhanced these traditional algorithms to have their best possible performance on single-processor computing platforms. These algorithms are still slow, and most of the power system computational analysis is limited to be off-line, which calls for the submission of high-performance computing application.

Traditionally, the Newton-Raphson algorithm has been the core algorithm for well-determined power flow equations. This algorithm is excellent for a single processor computing platform, and it works well in traditional computing environments. However, when combined with the direct solver of the underlying system of sparse linear equations, its formulation makes it difficult to parallelize for the dominant computing platforms (e.g., commodity computer clusters). By contrast, other algorithms such as Conjugate Gradient (previously viewed not as efficient as the Newton-Raphson algorithm) is inherently more suitable for parallel processing.

Besides solving well-determined power flow equations, optimization is another important aspect for power system computation. Optimization has found applications in areas of optimal power flow, state estimation, locational marginal price, and power system economic dispatch. Least square algorithms have been popular for state estimation, which intends to determine current system status in a real-time manner and serves as the basis for contingency analysis to predict system status when the system is constrained to outages. More recently, the results of state estimation are being applied to locational marginal price calculations for market operations. These calculations influence the amount of money that exchanges hands in the market. Optimization algorithms were studied and evaluated in this project, and new algorithms were developed as needed.

After three years of investment, this project results in a novel set of computational algorithms and capabilities with implementation on high-performance computing platforms for grid operations. The performance of these algorithms has been demonstrated with actual power system data. These capabilities are expected to enhance power system computational performance significantly (with higher computational efficiency and better functionality), enable real- or even faster-than-real-time simulation (which is not possible otherwise), and revolutionize power system planning, monitoring, and control to bring higher reliability and better asset use in the power industry.



(a) Today's static and slow operation

(b) Static but fast operation

(c) Dynamic and fast operation

Transformation of power grid operations.

Predicting the Impact of Climate Change on U.S. Power Grids and Its Wider Implications on National Security

Pak C. Wong, Lai-Yung Ruby Leung, Ning Lu, Mia L. Paget, James Correia, Wei Jiang, Patrick S. Mackey, Z. Todd Taylor, Yulong Xie, Jianhua Xu

◆ This research extends modeling theories derived from climate, energy, social, and security domains to predict viable future technosocial scenarios for policy-makers to formulate a coherent unified strategy toward building a safe and secure society. ◆

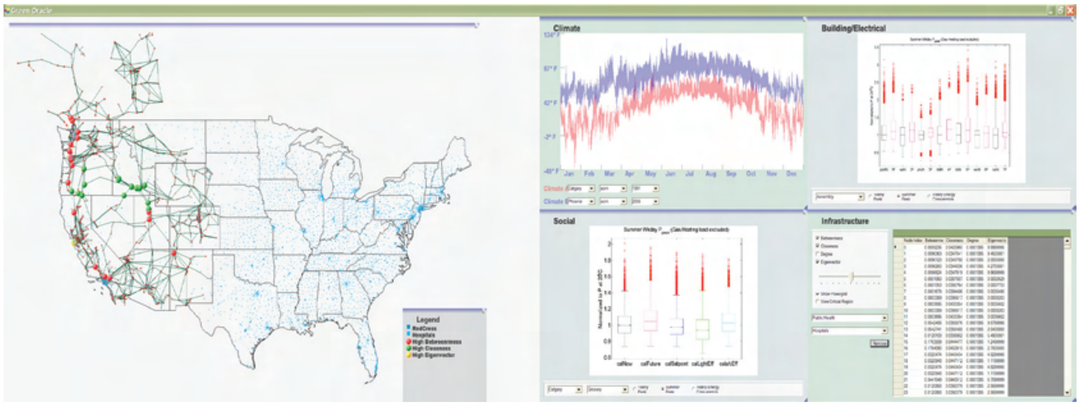
We model and predict the impact of climate change on U.S. power grids and the wider implications on society (such as economic and demographic changes) and national security (such as critical infrastructure protection). An example of climate change and its impact is increased atmospheric temperature, which in turn increases electricity consumption. Increased temperature affects precipitation, which changes the natural hydrological process and thus hydroelectric generation, and it also influences wind electricity generation. Together, these forecasted energy demands could adversely affect the U.S. power grids and cause a widespread outage. If such an outage persisted, it would impair the ability of our entire critical infrastructure to perform and could potentially cripple our society. Our work will investigate the potential impact and implications of these changes to society in the next 50 years from both a technical and social perspective.

The research and development activities of this project are conducted and coordinated in a sequential fashion. The lead components are completed to a degree that provides sufficient groundwork for the next component to be initiated before returning to refine and enrich the component models.

Thus far, we have accomplished the climate analytics work on temperature modeling. We also finished most of the building energy simulations that are required for the power grid simulation. On the social study front, we focused on the impacts of demographic and technological changes to the results of our study. A preliminary visual analytics system prototype has been developed to guide analysis among the domain components and to present results. These allowed us to finish the first simulation of climate change's impact on the power grids based on a so-called typical meteorological year setting. The results suggested a potential vulnerability of western power grid in the southwestern U.S. in the next 50 years. The screenshot shows our dual-screen visual analytics system, which allows users manipulate the model parameters of all four domains on the right and at the same time analyze results of the changes on the left of the display. These accomplishments are critical to achieving the project's major goals.

We have so far made progress on all four domain components. At the end of the first year of the project, the linkages among the components are not fully established; however, individual results have already revealed possible future social and technological issues. When all the pieces are connected, we can simulate the cascading impact of the power grid vulnerabilities to the other critical infrastructures such as energy pipelines, communication grids, and transportation networks. Some of the results have been submitted to peer-reviewed journals and conferences.

In FY 2009, we will continue investigating both technical and social issues that drive our model and develop a working user front-end to facilitate the integration of evidence and arguments generated from different model domains. Among the project's main goals is to integrate the domain model theories that we have developed so far into the interactive system. We will extend our climate scenario from a typical meteorological year standpoint to more devastating situations such as extended heat wave global warming scenario. From the social analytics side, we will investigate the impact on demographics changes and building stock projection of 10 major western U.S. cities. Our power grid analytics model will then generate more accurate scenarios based on these changes in the next 50 years.



A screenshot of our visual analytics front-end.

Prussian Blue Analogues and Interpenetrated Metal-Organic Frameworks for CO_2 Capture

Praveen K. Thallapally, B. Peter McGrail, Radha Krishna Motkuri, Carlos A. Fernandez

◆ We propose to design and develop low-cost, solid-based sorbents that capture CO_2 selectively from combustion systems that are superior to existing commercial technologies. If successful, these sorbents can be envisioned as the alternate to MEA and Selexol process of CO_2 separation applications. ◆

Our interest in Prussian blue and integrated metal-organic framework materials has been stimulated by recent literature by Long et al. and others, who have shown that these sorbents store a couple of weight percent of H_2 at 77K and 760 torr. The isosteric heat of adsorption for H_2 is 7 kJ/mol, which is 40% higher than typically observed in organic and metal organic solids. The small pore sizes, large isosteric heat of adsorption, and the capability to engineer the adsorption sites in these materials make them potentially promising materials for CO_2 capture.

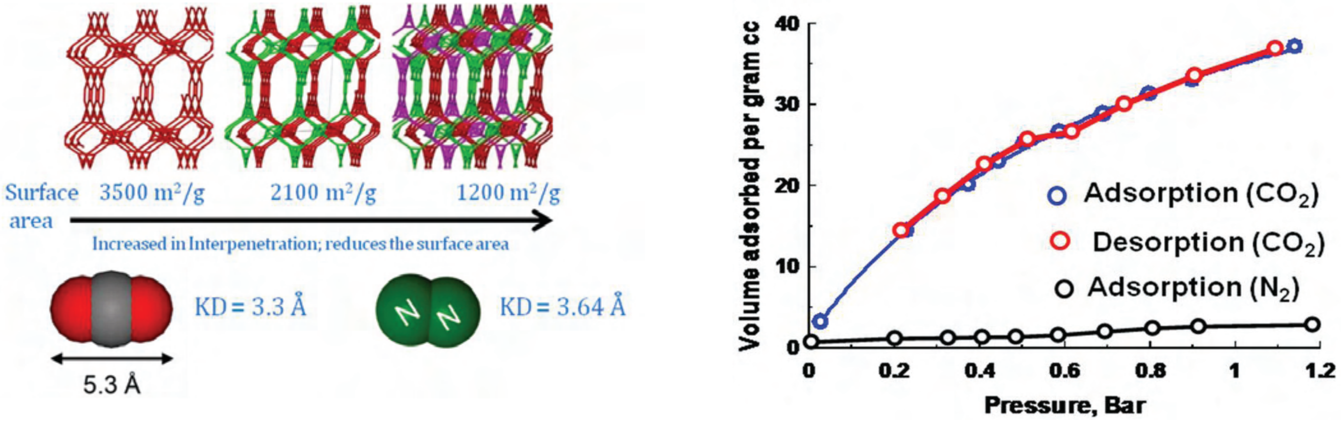
The advantages of these materials include high wt% of gas uptake, high thermal stability, adjustable chemical functionalities, extra-high porosity, and so on. The most prolific way to design the metal-organic frameworks is to employ multidentate ligands, such as carboxylates, to arrive consistently at more rigid networks with large surface area and high gas uptake capacity. Therefore, we would like to design and synthesize these solid sorbents for CO_2 removal applications. Once synthesized, we will obtain the basic characteristics of the Prussian blue analogues and metal-organic frameworks that look attractive in terms of 1) identifying variants that maintain higher loadings up to approximately 330 K, and 2) investigating material costs and the applicability of direct contact heating with steam or hot water for desorption. We will study synthesis methods to achieve a high synthetic yield to reduce the manufacturing cost for bulk quantities.

Most metal-organic frameworks have been deliberately designed with very large pore sizes or channels to achieve maximum loadings. While effective, the penalty is again lack of selectivity, which is required for gas separation applications. To approach this problem, we have proposed solid sorbents that interpenetrate in the solid-state, leaving smaller voids that selectively capture CO_2.

Materials based on Prussian Blue and integrated metal-organic frameworks led to two papers on CO_2 separation using solid sorbents that resulted in the cover art for the publications.

During FY 2009, we plan to explore the porphyrin-based solid sorbents that has the zeolitic topology for CO_2 separation applications. We will perform the following functions with these zeolitic sorbents:

- Synthesis of metal-organic porphyrin zeolitic sorbents
- CO_2 uptake and release measurements and other physical characteristics of synthesized materials
- Demonstrate uptake of CO_2 at flue gas conditions
- Demonstrate absorption and desorption properties of the synthesized materials at various temperatures
- Evaluate the feasibility of sorbent preparation at the commercial scale
- Effect of trace contamination on synthesized sorbents.



Interpenetrated metal-organic framework for CO_2 separation applications (right). CO_2 and N_2 uptake measurements of the same material at one bar shows significant selectivity toward CO_2 compared with N_2 (left).

Self-Correcting Controls for Heating, Ventilation, and Air Conditioning Systems

Srinivas Katipamula, Michael R. Brambley

◆ Commercial buildings in the U.S. are poorly operated and maintained, resulting in increases in energy consumption of up to 30 percent. While periodic commissioning (commissioning) can help alleviate the deficiencies with traditional operations and maintenance, the cost of manual commissioning has limited the diffusion of it in the commercial buildings sector. Automated commissioning and self-correcting controls could both substantially reduce the cost associated with commissioning but also help ensure persistence of efficient operations. ◆

Several studies have shown that poor operations and maintenance practices in commercial buildings lead to energy waste and emissions penalties of 10 to 30 percent. If these operating problems were eliminated, the benefits could be on the order of up to 4 quads of energy and up to 240 million metric tons CO_2 per year in the U.S. alone. Performance problems usually result from errors in installation and operation of complex building heating, ventilating, and air-conditioning (HVAC) systems and their controls. Because of their complexity, high-performance and net-zero-energy buildings may be even more susceptible than average commercial buildings to efficiency degradation from inadequate operations and maintenance.

Commissioning can help alleviate operations and maintenance problems. Despite all the benefits, commissioning comes at a cost (PECI 1997). A recent report by Quantum Consulting (2003, pp. 1-3) on commissioning in public buildings states, “While the concept of commissioning is increasingly accepted, there are still barriers – particularly with regard to cost – to implementation of the kind of thorough, independent third-party commissioning that is necessary for the full benefits of commissioning to be realized.” Only a small fraction of new construction and a very small fraction of existing buildings have been commissioned. Even when performed, pressures exist to keep costs down, which in some cases limits the depth to which the commissioning is performed. Furthermore, the corrections made during commissioning do not persist. A key solution to reduce the labor cost and ensure persistence of commissioning benefits is to automate as many of the commissioning processes as possible through self-correcting controls.

The objectives of this research are to create a testbed to support development of self-correcting controls for HVAC systems and to demonstrate that such controls are feasible and practical through tests and demonstrations in a laboratory test facility with real control systems. A secondary aim is to position PNNL at the forefront of developing technology for the next generation of building control systems. The expected outcomes of this work include the following:

- Development of a testbed framework to test and demonstrate self-correcting controls in a laboratory environment.
- Self-correcting controls for a selected set of air handling unit (AHU) and control problems (e.g., faults with temperature sensors, dampers, valves, and heat exchangers).
- Development and demonstration of PNNL capabilities in developing self-correcting controls for HVAC systems and positioning the Lab to lead future funded development efforts.
- Availability of a demonstration of the “real-world” feasibility of self-correcting controls for presentation to potential funders of research, development, and demonstration projects.

In FY 2008, a test bed was created to develop, test, and demonstrate self-correcting controls in a laboratory environment. Space was acquired and an AHU was set up and selected instrumentation and controls were installed. A chiller was acquired but not integrated with the test bed. In FY 2009 the chiller will be fully integrated with the AHU and additional instrumentation and additional controls will be installed to make the lab fully functional.

Self-correcting controls for a selected set of AHU and control problems were also initiated. A software framework to deploy and test self-correcting control algorithms has been developed using temperature sensor problems as a basis. In FY 2009, additional work is needed to test and validate the framework and to demonstrate self-correcting controls for an additional set of AHU control problems. This test and validation will occur after the chiller is fully integrated with the AHU (previous outcome).

Significant progress has been made in developing self-correcting controls. Progress has also been made to demonstrate the “real-world” feasibility of self-correcting controls. With completion of this laboratory setup in FY 2009, this outcome will be fully accomplished.

By project end, we expect to publish at least one journal article on the results of this research.

Tailoring of Fischer-Tropsch Synthesis Product Distribution Using Monolith Catalysts

Yong Wang, Wei Liu

◆ This project aims to develop a compact, modular-type Fischer-Tropsch (F-T) reactor concept with monolith-structured catalyst beds to replace the conventional catalyst fine-dispersed slurry or pellet-loaded fixed bed reactors with significant improvement to temperature control, product selectivity, catalyst use, and scale-up. ◆

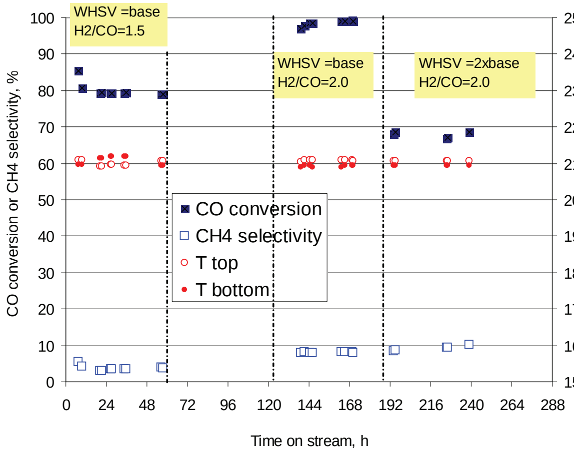
Syngas can be derived from various energy and/or feedstock resources such as biomass, hydraulic electricity plus CO_2, remote natural gas, solid wastes, and coal. The F-T process can convert the syngas into clean fuels and chemical feedstock. However, the current F-T process is associated with high capital and energy costs and is thus cost prohibitive for the application with processing capacity by orders of magnitude smaller than the typical refinery/petrochemical complex. This project explores the novel concept of controlling product distribution in Fischer-Tropsch synthesis (FTS) via mass transfer reduction. Our research strategy is to reduce diffusion length and minimize re-adsorption of olefins to shift FTS product distribution to a narrower carbon range (e.g., gasoline and/or diesel) by coating a thin layer of FTS catalyst on monolith structures. Our work is built on previous expertise established at PNNL on developing engineered Fischer-Tropsch synthesis catalysts for microchannel reactor. This project will enhance PNNL's capability in the field of coal to liquid conversions by bringing together the existing strengths in the FTS catalyst, nanoscale catalyst synthesis, novel reactor design, and monolith catalyst integration.

This project provides step-out approaches to the new reactor design concept to address this problem. The scope of this project includes 1) coating of proven F-T catalyst composition on the commercial ceramic monolith substrate, 2) making new reactor designs and developing catalytic reaction testing protocols, and 3) testing catalytic reaction of new design concepts and data analysis. Making uniform F-T catalyst coatings on the monolith and loading and testing such catalyst structures in the existing F-T reactor testing systems are not easy; constant innovation and dedicated effort are required.

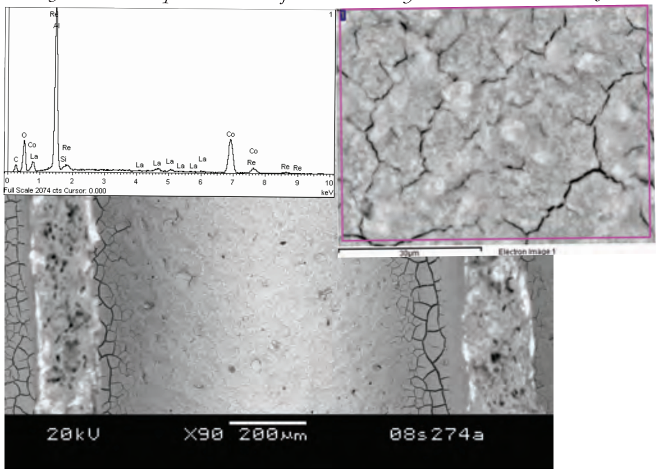
Significant project accomplishments are summarized as follows:

- Developed catalyst coating methods and improved catalyst testing protocols.
- Demonstrated excellent temperature control in the non-microchannel reactor configurations (e.g., monolith catalyst bed concept).
- Demonstrated superb performances in terms of the combination of high productivity, low methane selectivity, and stable catalyst performances.

Steady-state conversion profiles are shown under typical F-T reaction temperatures and pressures of a structured catalyst bed that has characteristic heat transfer dimension of ~10 mm and a bed length of ~150 mm. The temperature differential between the entrance and exit point of the catalyst bed was less than 2°C. At stoichiometric H_2/CO feed ratio of 2, ~95% CO conversion and fewer than 10% CH_4 selectivity were obtained. By contrast, ~24% CO conversion and 8% CH_4 selectivity were obtained with the same catalyst in the crushed particle form under the same reaction conditions. The excellent results achieved with the structured catalyst bed are unprecedented.



Steady-state FT reaction performances.


Catalyst metal composition is confirmed　*Catalyst-coated substrate surface*

F-T Reaction Performance.

Thermodynamic Model to Predict Thermal Behavior of Lithium Ion Batteries

Jason Zhang, Vish V. Viswanathan, Rick E. Williford

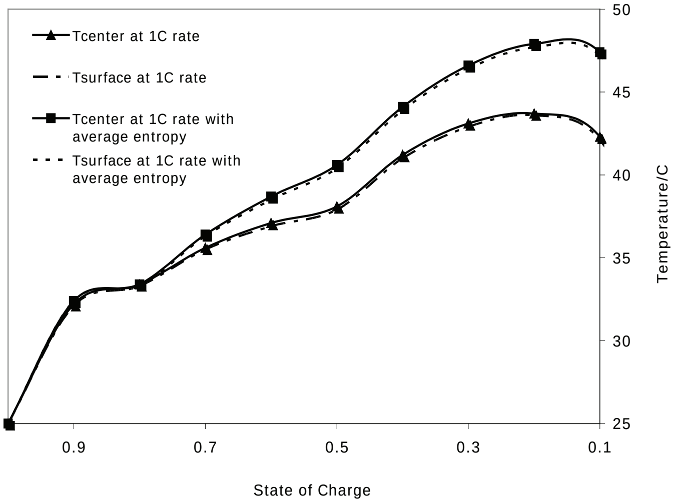
◆ High-power secondary batteries for plug-in hybrid electric vehicle applications generate much more heat during rapid charge/discharge cycles at high current levels. It is necessary to develop a versatile model to predict more detailed thermal behavior for a battery with different cathode and anode materials. Such an improved model will help industry developers design a new-generation battery that will minimize heat generation and fluctuation, thereby significantly reducing heat-induced failures. ◆

In a model established two decades ago, Benardi et al. described a general energy balance equation for battery systems. This system of equations launched cell temperature prediction and heat generation resulting from electrochemical reactions, phase changes, mixing effects, and Joule heating. Pesaran et al. investigated a three-dimensional model thermal battery performance and simulated thermal behavior of a cylindrical lithium (Li)-ion battery, assuming that the core material (cathode/separator/anode) consisted of a homogenous material with average properties for resistivity and thermal conductivity. In these studies, it was assumed that core material consists of a homogenous material with average but anisotropic properties for resistivity and thermal conductivity. These models can be used only to simulate the average behavior of existing batteries and cannot predict thermal behavior of batteries with new components. Therefore, a versatile model based on the fundamental properties of electrode materials needs to be developed that can predict the internal temperature as a function of battery chemistry, charge state, power rate, and battery geometries. This model will help the industry design a battery with minimum heat generation and fluctuation, therefore largely reducing heat-induced failures.

The entropies (ΔS) in various cathode and anode materials and complete Li-ion batteries were measured using an electrochemical thermodynamic measurement system. Cathodes and anodes were mixed with 85% active material, 10% PVDF, 5% carbon black, and cast on aluminum and copper foil, respectively. Customer-coated cathode and anode films purchased and used for entropy measurement. To measure entropy changes in cathodes or anodes, the latter were assembled in a Type-2325 coin cell with a 0.75 mm thick Li-foil anode (Aldrich), a Celgard 2501 polypropylene separator and electrolyte (1M $LiPF_6$ in EC/DMC [Merck]) using a coin cell crimper. Complete cells with $LiCoO_2$-based cathodes and graphite-based anodes were assembled using a similar procedure by replacing Li metal with the graphite-based anode. Large prismatic Li-ion batteries (using modified $LiCoO_2$/graphite) with a nominal capacity of 4.5 ampere-hour were used for temperature measurements under different conditions.

A two-dimensional thermodynamic model based on the fundamental properties of individual electrodes was established to obtain the transient and equilibrium temperature distribution of Li-ion batteries. The thermodynamic properties (entropy change, ΔS) of cathodes and anodes materials measured in this work were used to simulate the thermal behavior of batteries. The results from theoretical simulations were compared to results obtained in experimental measurements. We found that the detailed shape of the entropy curves strongly depends on the materials manufacturer even for the same nominal compositions. $LiCoO_2$ has a larger entropy change than $LiNi_xCo_yMn_zO_2$, which is more thermodynamically stable. The temperatures around the positive terminal of a prismatic battery are consistently higher than those at the negative terminal. When all other simulation parameters are the same, simulations that use a battery-averaged entropy tend to overestimate predicted temperatures compared to simulations that use individual entropies for the anode and cathode.

We propose to continue this work in FY 2009 to extend our two-dimension model into a three-dimensional model that can more accurately simulate the practical batteries. The resulting model will be a powerful tool to aid the design of high-power high-energy batteries for PHEV applications.



Temperature profiles in a $LiCoO_2$/C battery when it is discharged at 1C rate. The figure shows that using a battery-averaged entropy in a simulation tends to overestimate the predicted temperatures compared with a simulation that uses individual entropies for the anode and cathode.

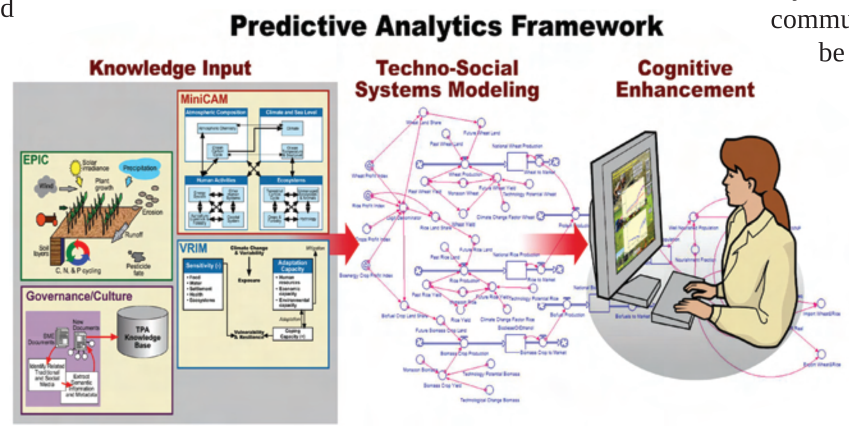
Vulnerability of Food Security and Energy Infrastructure to Climate Change and Terrorism

Elizabeth L. Malone, R. Cesar Izaurralde, Larry G. Morgan, Allison M. Thomson, Son H. Kim

◆ This project is integrating knowledge domains in energy, food, and national security, which are tightly interconnected but usually considered separately. Modeling the connections allows analysts to examine a wider set of outcomes to decisions with the purpose of promoting energy security, diversifying crop production, or easing trade barriers. ◆

Although a need for integration has long been recognized, modeling social and physical variables together has proven difficult. Time and spatial scales, diverse units of analysis, and quantitative and qualitative issues have proven formidable barriers. Even integrated assessment models are largely limited to physical data (energy and in some cases land-use and agricultural) with economics substituting for social data. The objective of this project is to integrate the domains of knowledge about a region. We are drawing 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 productivity) and ecosystems, and 3) VRIM, an indicators model that produces comparative analyses of social and environmental resilience to climate change. We are adding governance/civil society/cultural data that are being modeled as rules of behavior.

This project is building capability in the area of integration and predictive analytics. Analysts will be able to see and account for interactions among different domains in evaluating the effectiveness of candidate actions. The analyst would need to either have this knowledge outside of a model focused on emissions mitigation and economics or consult with a wide array of experts. The integration of multiple knowledge domains thus improves the quality of the analysis and enables new insights.



The Indian subcontinent (India, Pakistan, Bangladesh) was determined to be the project's focus as an area both highly vulnerable to climate change and important geopolitically. The project team identified historical data and obtained model data and outputs from the three PNNL models above relevant to the Indian subcontinent for this project as well as qualitative (text-based) data to address questions about food, energy, and national security. The team established a structure and methodology for integrating existing model data and results, and then built and demonstrated a prototype modeling space in STELLA® to address questions about the tradeoffs producing biofuels in India.

Our project team established a knowledge repository 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 the knowledge repository. This project's team derived from the knowledge repository sources governance and civil society characteristics to be used in constructing the new model. Our team also established a gaming concept, including a narrative of the game and definitions of the players.

To overcome various barriers to integrating knowledge from different disciplinary areas and domains, the most promising approach was to design a new model using a systems approach. With input from peers and prospective users/clients, the research team will conduct a review of the prototype and develop it further, adding detail on competition for land to grow various types of crops. Input from those who would run or use results from the model will be crucially important to guide development. We will continue to develop a mechanism for using social data harvested from the Internet to update variables and variable values. We will also actively engage in integration and evaluation activities.

Future outcomes and benefits will include demonstrating the usefulness and relevance to users within the national security and climate change analytic communities. Analysts will be able to use a techno-social modeling tool that shows how actions in one domain (e.g., a policy to increase production of biofuels) have consequences in other domains (food security, energy security, climate mitigation).

Engineering and Manufacturing Processes

Delivery of Calcium Polysulfide to Hanford Deep Vadose Zone for Cr(VI)/ Tc-99 Remediation

Lirong Zhong, Z. Fred Zhang, P. Evan Dresel

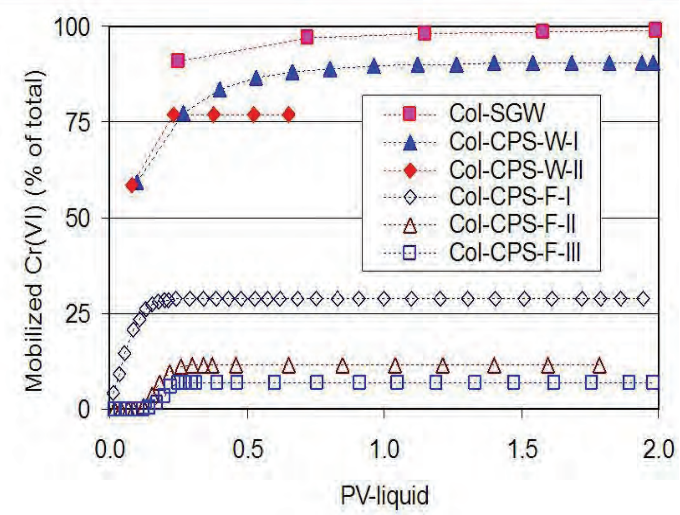
◆ This project is aimed at developing the foam-delivery technology for the distribution of remedial amendment, calcium polysulfide (CPS), to the Hanford Site deep vadose zone for in situ immobilization of chromium [Cr(VI)] and technetium-99 (Tc-99). ◆

The remediation of Cr(VI) and Tc-99 contamination at the Hanford Site vadose zone is a critical need. Water-based remedial amendment delivery to the deep vadose zone is facing significant technical challenges, such as uneven fluid flow and the spread of mobile contaminants from the vadose zone to aquifer. The foam-aided amendment delivery approach has the potential to resolve the uneven remedial fluid distribution and contaminant mobilization/spreading issues. The objectives of this project are to: 1) identify a surfactant-CPS system that can produce foams stable enough for delivery/injection, 2) demonstrate that the foam-aided delivery technology is capable of delivering CPS to the vadose zone with a uniform sweeping over heterogeneous contaminated zones, 3) show that the significant mobilization Cr(VI)/Tc-99 front commonly encountered in water-based delivery, which causes contamination spreading and threatens the underlying aquifer, can be eliminated or minimized in the foam-aided delivery, 4) verify that Cr(VI) and Tc-99 in the deep vadose zone can be immobilized via reductive reactions with CPS, and 5) develop procedures and parameters for a field demonstration.

In FY 2008, a series of batch and column experiments were conducted to achieve the goals. Batch tests were conducted to select the foam-generating CPS-surfactant solutions, determine the solution foamability and the reducing 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 the foam delivery of CPS to sediments under conditions similar to field vadose zone, study the foam transport and interaction with sediments, and determine the extent of Cr(VI) immobilization using this novel delivery approach. Mathematical simulation studies on foam flow in porous media were also carried out. CPS-containing foams with high reducing potential were prepared based on the batch tests. The foam stability decreased when the foam quality (the ratio of gas volume to total foam volume) increased and when the CPS concentration in the foaming solution increased.

Sediment reduction by foam-delivered CPS was observed in the columns when the foams were generated using nitrogen; sediment reduction was not observed when the foams were generated using air. Significant mobilization of Cr(VI) from sediment columns occurred when CPS was delivered in aqueous solution. The Cr(VI) mobilization was minimized in column tests when CPS was delivered by foams, resulting in significant Cr(VI) in situ immobilization. These results demonstrated for the first time that foam injection can be successfully used for CPS delivery and that foam-delivered CPS can be applied for Cr(VI) immobilization in contaminated vadose zones. A mathematical expression for foam flow in porous media was developed.

Further studies are essential to address the following critical issues—first, the immobilization of Tc-99 by foam-delivered CPS has to be demonstrated. Reoxidation of immobilized Tc-99 was reported, and the significance of Tc-99 remobilization in the vadose zone by infiltration of oxygen-containing water demands an evaluation. Second, the enhanced sweeping over heterogeneous system is an important characteristic of foam flow, but it has not been demonstrated under vadose zone conditions. Such a demonstration has an important value for the remediation technology development. Third, the transport retardation of the remedial amendment, CPS, is a critical factor affecting the remediation performance; an evaluation on this factor is in demand. Fourth, although a mathematical description of foam flow in porous media has been developed, a numerical model is required for larger-scale remediation performance simulation and prediction.



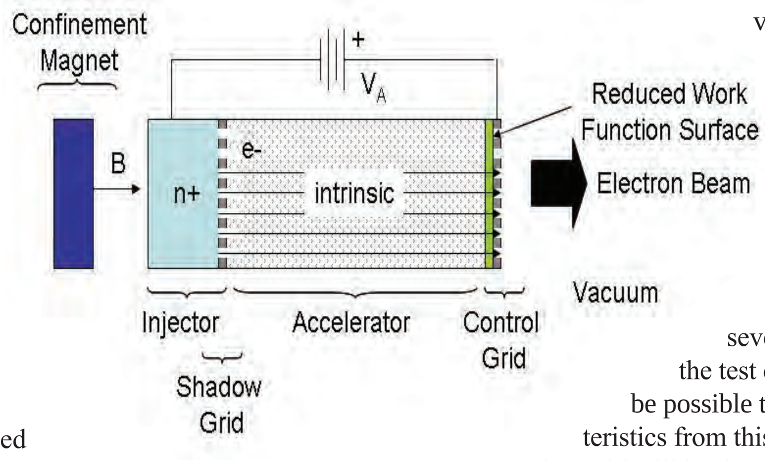
Cumulative mass of mobilized Cr(VI) in effluent from column tests: a comparison of calcium-polysulfide (CPS)-containing foam flush (Col-CPS-F-I, II, III), CPS solution flush (Col-CPS-W-I, II), and synthetic groundwater flush (Col-SGW). Themajority of Cr(VI) was immobilized in sediment when CPS was delivered by foam injection.

Development of a Ballistic Electron Microfabricated Cathode

Kyle J. Bunch, Lax V. Saraf, Hong (Amy) Qiao

◆ A solid-state cathode with a high brightness will serve as an enabling technology for many different fields. It could be used in high-contrast flat panel displays, conventional vacuum microwave/millimeter-wave devices, or next generation vacuum microelectronic devices. ◆

Current research in this field focuses on tips that create emission from sharp points of diamond. In this project, the approach is to inject electrons into an intrinsic diamond region and accelerate them to overcome the work function of the diamond material. We aim to increase the electron density over that of field emission tips. One of the project issues is to make a solid-state cathode with practical emission densities. As has been the approach for the last 30 years, using a field emission approach results in poor average emission densities. For the first time, we will use ballistic transport within a material to overcome the work function of the material. Technical achievement expected within this project is a demonstration of using ballistic transport within a material to create a cathode superior to current approaches (i.e., field emission cathodes).



The ballistic electron cathode.

During FY 2008, we looked at the current state of the art in field emission cathodes and selected three materials as promising: 1) diamond on doped silicon, 2) silicon carbide (SiC), and 3) gallium arsenide. The material must have a combination of high breakdown field strength, long electron mean free path (for ballistic transport), and practicality for fabrication. Using EMSL facilities, we developed capabilities to deposit diamond films on silicon using an oxygen/acetelene torch. The techniques used to deposit diamond were presented and published in the nanotechnology conference.

Design and fabrication of SiC demonstration wafer and Ab Initio simulations of diamond band structure. Cree has fabricated two silicon carbide wafers with an intrinsic SiC layer for use in ballistic electron acceleration. These will be tested and then modified to have an acceleration grid deposited on their surface. The simulations were intended to determine the work function and suitability of diamond for use in cathodes. The results verify the experimental results of other researchers.

The chamber has been put together to take a sample down suitably to a reasonable vacuum level. It has also been modified to bring in a high voltage source and is being modified to measure a small current safely at a high voltage floating potential.

During FY 2009, the chamber will need to measure microamperes of current and safely stand of several kilovolts of power. Once the test chamber is complete, it will be possible to measure emission characteristics from this material. Also, an acceleration grid will be deposited and the wafers tested again to demonstrate project principles. For fabricating diamond, we currently have the silicon wafers ready for deposition; once fabricated, they will be tested and compared with the SiC design. The research under this project is unique and will be suited for a journal publication.

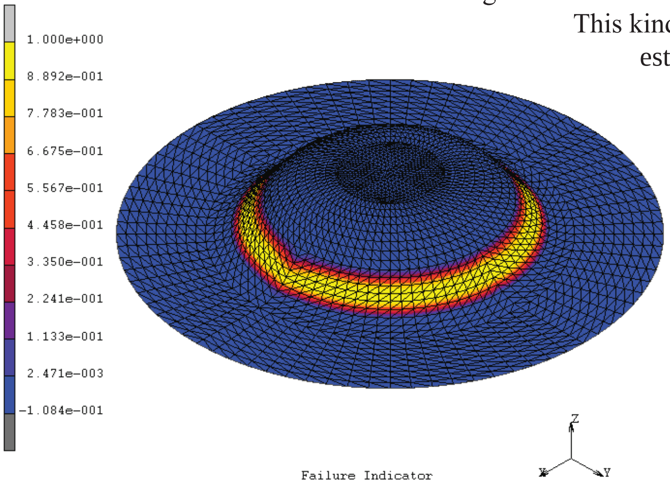
Forming Prediction of Lightweight Alloys Using an Inverse Approach

Ba Nghiep Nguyen, Satish K. Bapanapalli

◆ This project has developed a computational tool using a multi-step inverse approach to metal forming to predict quickly and accurately the formability of lightweight magnesium or aluminum alloys. ◆

The rapid production of high quality, lightweight, inexpensive alloy components is one of the most important goals of the automotive industry. Computational models and tools are needed to assist in the forming process to avoid costly and time-consuming trial-and-error practices. In metal forming, it is essential first to predict whether a part can be formed and determine optimum process parameters. Conventional forming technologies for magnesium alloy sheets are restricted because of poor formability of the materials at room temperature, which is caused by the hexagonal close-packed structure of the material. However, magnesium alloys exhibit increased formability at higher temperatures (200-300ºC) due to the activation of additional slip planes.

Predicting magnesium alloy formability at desired forming temperatures is a key element for successful part formation. To achieve this objective, a multi-step inverse approach is an efficient, valuable method in the pre-design stage. The inverse approach can provide quick, reasonably accurate estimates of stress, strain, and thickness distributions as well as material formability compared to the accurate but time-consuming and costly incremental methods. The INAPH (INverse APproach to Hydroforming) finite element code for tubular hydroforming prediction was extended and enhanced to analyze press forming of lightweight materials for automotive applications. This code, which responds to the need of optimum design of lightweight materials for energy efficiency, enables engineers to assess material formability.



INAPH's failure prediction for forming a circular AZ31 blank. Failure is predicted to occur when the failure indicator is equal to 1. The failure indicator is defined by the ratio of the damage variable to its critical value.

Work performed during FY 2007 involved modifying INAPH to account for the press-forming features, such as the punch and blank holder forces actions and friction contacts between the tool, sheet, and die. A multi-step approach to press forming was developed in INAPH by constructing a number of assumed intermediate configurations between the initial and final shapes using a depth division method. This approach partially accounts for the loading history and thus improves the accuracy of stress prediction in deeply drawn parts. A stress-based failure criterion and functional representation of the material stress-strain laws were introduced to predict failure during forming at various temperatures.

In FY 2008, work included enhancement of the developed multi-step inverse approach to build more realistic intermediate configurations, implement a continuum damage constitutive model into INAPH to predict damage and failure during forming more accurately, and perform forming analysis of magnesium alloy sheets at various temperatures using enhanced INAPH. In addition to the depth division method developed in 2007, intermediate configurations were built using a sequential quadratic programming technique or a novel node relocation method. This process minimizes the sheet metal surface area subject to constraints, while the node relocation method quickly estimates intermediate configurations based on tooling geometries and adjustments of nodal positions. This kind of node relocation technique to estimate realistically intermediate configurations for deep-drawing cases is a completely novel and unique feature of INAPH. Due to the limited formability of magnesium alloys, it is important to estimate realistically the intermediate configurations so that a mechanics approach can be explored to predict damage accumulations that can cause sheet rupture during formation.

An elastic-plastic damage constitutive law was implemented in INAPH using the modified Hill's criterion and deformation theory of plasticity to describe the behavior of magnesium alloys. Damage was captured by a variable that governs equivalent stress. A damage-plasticity coupled approach was developed for the integration of constitutive equations. The computed equivalent plastic strains and stresses for inter-mediate configurations were used to predict resulting damage accumulations during formation. Using this continuum, the enhanced INAPH damage mechanics multi-step inverse approach was applied to predict forming of AZ31 magnesium alloy sheets at room and higher temperatures. INAPH's predictions agree with experimental data found in the literature.

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 the impacts of intermittent renewable generation on the 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 negative impacts, including optimizing generation portfolios and dispatch procedures. ◆

Wind and solar energy resources produce no air pollutants or greenhouse gases compared with fossil-fuel power plants. They also help to reduce existing U.S. energy sector dependency on foreign energy resources. The U.S. federal government, DOE, and individual states are pursuing aggressive programs to increase significantly the share of renewable resources in the total generation portfolio. Adding more renewable generators to the grid and their priority dispatches are supported through the tax incentives (e.g., through the Production Tax Credit), States' Renewable Portfolio Standards, Qualifying Facilities provisions, and other means. However, the integration of wind and solar energy into the power system involves complicated and sometimes controversial processes. Due to their inherent intermittency, the variance of load seen by other generators can be dramatically increased. At the same time, the new thermal generation additions in many areas are mainly combined cycle units that provide a high level of efficiency but have steep heat rate characteristics. These units have a limited cycling capability due to the wearing problem, start-up cost, and emission; they cannot be dispatched below 70% (or 50% for some new designs) of their capacity due to efficiency and other considerations. As a result, uncoordinated and poorly researched integration of intermittent resources could significantly reduce the efficiency of these thermal units, causing additional wear-and-tear problems, resulting in uneconomical unit commitment and dispatch patterns and increasing emission and other negative environmental impacts of the other units.

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 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. Development of these capabilities support key DOE missions in reducing the environmental impacts from energy production and use, and cost effectively improving the energy efficiency of the United States, which in helps to develop the economy.

The project has been planned to have two phases. The first phase, conducted in FY 2008, includes reviewing, analyzing, and identifying national (and international) experience in the area of smooth integration of intermittent resources, and the generation development plans and Renewable Portfolio Standards in the Pacific Northwest and California. In FY 2009, we will build models for various types of generation units as functions between efficiency, emissions, costs and power output.

The outcomes associated with the work performed during this fiscal year include the following:

- Surveying operational impacts of intermittent resources as well as mitigation measures.
- Collecting data and understanding power plant operations as well as building generator and power system operation process models from industry.
- Developing a framework of a power system operation process simulation program, including a simplified generation dispatch module with in-hour balancing module and necessary generator models.
- Developing a methodology that includes a high-level description of the operation process simulation program and how to use it to evaluate the impacts of intermittent resources on energy production cost and emissions of dispatchable generations.
- Investigating thermal generator models, including how to calculate emissions and formulation of the cost function.

During FY 2009, we will improve models of thermal and hydro generators using data collected from the industry, complete coding of the simulation program that simulates unit commitment and economic dispatch, load following and regulation processes, evaluate the efficiency of generation portfolios and dispatches with different level of wind in the system, build models for new balancing resources (energy storage device and demand response), complete a simulation program for unit commitment and dispatch process with the new balancing resource models integrated, and finish recommendations for plans on integrating the new balancing resources.

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, illustrating 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. The objective of this work 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 will be validated using available data.

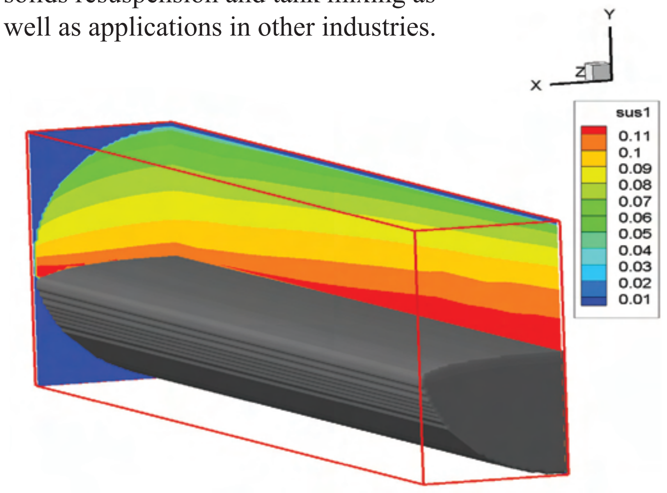
The simulation approach is based on lattice methods (lattice Boltzmann/lattice kinetics). Distribution functions containing information about the pressure tensor streams to adjacent lattice sites. The summation of these quantities results in equations solved for mass, momentum, and scalar transport. The method depends only on local information and scales nearly linearly with the number of computer processors.

Solid-liquid multiphase flow models were incorporated 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 the 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. Simulation results were compared with data obtained from experiments performed using a particles ranging from nominal 10-100 µm in diameter and solid densities of 2-10 g/cc. The pipeline is operated at different flow rates, and the pressure drop is measured. At critical flow velocity, further decrease in flow results in an increased pressure drop due to sediment bed buildup within the pipe. The sediment height is determined by the equilibrium between the rate of deposition by hindered settling and the rate of erosion, which is a function of the turbulent shear stress at the surface of the sediment. Comparison of simulation results with experimental data showed very good agreement.

Work has begun on incorporating a thermodynamically-based chemical reaction model that is specifically targeted to systems with high ionic concentrations. In a separate task, work was done to augment the current pulse jet design with a model predictive control system. Use of such a controller will allow for independent pulse jet tube levels to be monitored and controlled in real time with the use of only pressure transducers. This allows for the possibility of safeguarding against pulse jet overblow conditions, asynchronous firing patterns, and direct control of the nozzle velocity/time profile while a pulse jet is firing. Activities scheduled for FY 2009 include the extension of this work to solids resuspension and tank mixing as well as applications in other industries.



Sediment and suspension solids concentration in a slurry transfer pipe below the critical velocity.

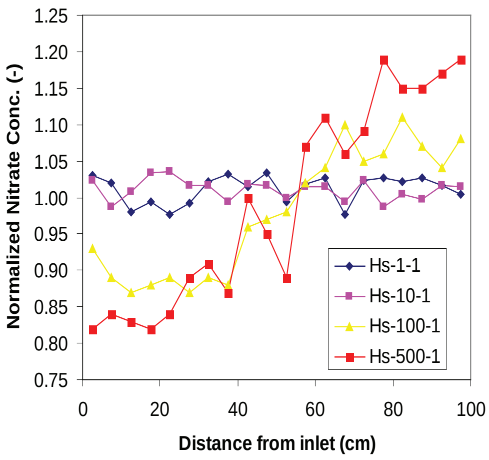
Soil Desiccation for Deep Vadose Zone Remediation

Martinus Oostrom, Michael J. Truex

◆ This project is evaluating the injection of dry air into a subsurface layer as a means of limiting the downward migration of contaminants to groundwater. ◆

Soil desiccation has been recognized as a potentially robust remediation process for the deep vadose zone because it is based on evaporation induced by air injection and extraction. Previous feasibility studies and expert panel analyses identified several technical issues as part of developing and applying soil desiccation to deep vadose zone treatment at the Hanford Site. The primary attribute of desiccation is the removal of excess moisture from the subsurface, thereby reducing the driving force for downward migration of water and contaminant solutes within the vadose zone and providing a capacity over time to limit the downward migration induced by surface water infiltration.

The purpose of this research is to improve our understanding of the soil desiccation process as a possible means of immobilizing contamination, specifically addressing key technical concerns related to the energy balance, osmotic effects, and potential for contaminant remobilization through rewetting after the desiccation period. This improved understanding will be derived from detailed laboratory flow cell experiments and numerical simulation. The data sets obtained from column and flow cell experiments and successful comparison with numerical simulation results using the Subsurface Transport Over Multiple Phases (STOMP) computer model simulator will increase confidence that the effectiveness of soil desiccation can be reasonably predicted, supporting future decisions about implementing desiccation for deep vadose zone remediation at Hanford. Without an experimental protocol addressing the outstanding technical issues, this relatively simple and cost-effective technique might not be considered for field-scale implementation.



For slow-moving desiccation fronts and high-solute concentrations (above 100 g/L), solute redistribution may occur in the soil moisture and in the direction of the gradient. Maximum concentration increases of ~20% were observed.

During FY 2008, we continued research to quantify energy requirements for the desiccation process and studied contaminant migration during desiccation. Including the consideration of contaminant transport, flow cell experiments are a first step in quantifying the capacity to limit downward contaminant migration as driven by water infiltration. One set of tests focused on osmotic effects due to variable concentration brines and potential high-concentration breakthrough of contaminants from rewetting after a desiccation event; another will target the effects of heterogeneity on contaminant transport in systems undergoing desiccation. Results of these studies have been submitted to the *Vadose Zone Journal* and presented in October 2008 at the Soil Science Society of America meeting.

A series of laboratory experiments in unsaturated heterogeneous systems was conducted to understand the impact of energy balance issues on soil desiccation. Tests were simulated using independently obtained hydraulic and thermal porous medium properties. In all experiments, the injection of dry air proved an effective means for removing essentially all moisture from the test media, where evaporative cooling generally decreased with increased distance from the gas inlet chamber. Additionally, fine-grained sands in the heterogeneous systems show two local temperature minima associated with the cooling. The first occurs because of evaporation in the adjacent medium-grained sand, where the second minimum is attributed to evaporative cooling in the fine-grained sand itself. Results were simulated accurately, indicating that proper physics were incorporated, and provided a unique data set to calibrate the STOMP code in the design of field-scale desiccation systems.

A second set of experiments examined the impact of salt concentration on desiccation. Columns were filled with moist sediments and various salt concentrations that were desiccated with various rates. Results strongly suggest that desiccation rate is not a function of salt concentration; a moderate concentration increase does not impact the process as desiccation rate is independent. However, the impact of the solute concentration front on rewetting and over larger distances in the subsurface still needs to be investigated. Subsequent experiments examining salt concentration on the rewetting processes are needed to determine how salt impacts the effectiveness of desiccation in mitigating water and contaminant migration in the vadose zone.

Materials Science and Technology

Accelerated Fuel-Cladding Test Methods and Tools

Charles H. Henager Jr., Charles F. Windisch Jr., Shenyang Hu, Howard L. Heinisch

◆ 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 save development time. This study will develop miniature and subminiature specimens to understand and predict fuel-cladding interactions for advanced nuclear reactors and new fuel forms. ◆

Innovative experimental tools and techniques plus computational models will accelerate fuels and materials qualification for advanced nuclear reactors such as those proposed under the Global Nuclear Energy Partnership programs. This study will develop miniature and subminiature specimens to understand and predict fuel-cladding interactions for advanced reactors and new fuel forms. The specimens will be designed to be fully instrumented fuel-clad test samples as in situ material “couples” using surrogate materials to evaluate the transport of mobile species from advanced fuel mixtures while allowing chemical and mechanical test data to be obtained during accelerated thermal or radiation exposure. Ion beams will be used for simulating fast neutron radiation damage together with radiation damage modeling. The data from this study will be used to provide the data in a qualified computational framework for others.

Based on PNNL expertise and experience in miniature specimen technology, we developed a miniature suite of test specimens and test methods to understand the complex interactions that occur between nuclear fuels and fuel-cladding materials. The interactions include high-temperature thermo-chemical reactions between volatile radionuclides and the metal clad, radiation damage to the fuel and cladding, fuel restructuring and swelling, fission gas release, helium embrittlement, metal hydride formation, liquid and gaseous embrittlement of cladding, cladding corrosion and phase stability, and cladding mechanical and thermal degradation. The same miniature specimens can be ion irradiated to simulate neutron radiation effects. Data from these experiments will be developed for inclusion into the FRAPCPON-3 fuel cladding behavior code.

Accomplishments during FY 2008 included the following:

- A laser Raman accelerated kinetic tool for 3-mm disks was demonstrated using alloy HT-9 in the form of 3-mm diameter disks
- Miniature tensile specimens of HT-9 FFTF heat alloy were fabricated and tested at elevated temperature in air
- A new phase field model of prototypical nuclear fuel gas bubble microstructure and thermal conductivity evolution was developed.

The laser Raman studies on HT-9 developed a unique kinetic signature using 3-mm disks of alloy HT-9 oxidized in the air for up to 6 hours at 700°C and demonstrated the ability to distinguish between oxide phases and layers. This is significant because HT-9 is one of the preferred alloys for advanced fuel cladding material. This process demonstrated the ability to perform accelerated chemistry studies on miniature specimens using thermal acceleration and short times and the ability to obtain kinetic data relevant to fuel-cladding interactions. Coated HT-9 disks were also measured, and key differences were easily observed that can be used to help determine the effects of fuels on cladding chemistry. A publication has been prepared and accepted for publication in the *Journal of Nuclear Materials*.

Miniature specimen mechanical property testing also began using the HT-9 alloy machined into miniature tensile specimens. We built a test apparatus for this testing and obtained excellent tensile data in air at ambient, 450°C, and 550°C for HT-9. This data will be used for correlations with other test methods. Further, the modeling task has developed a new phase field model for microstructural evolution of nuclear fuel suitable for prediction of thermal conductivity changes. The modeling task has also identified the major differences between neutron and ion irradiation damage and has brought together the tools necessary to understand and model these differences.

We are in the process of designing key experiments using ion beams at PNNL to simulate radiation damage in fuel cladding with surrogate fuel materials. These ion irradiations are well-suited for miniature specimens because ion ranges are small compared to neutrons, plus ions can accommodate accelerated testing because damage rates are much higher than neutrons. We intend to exploit these tendencies to design miniature tests that can be scaled to simulate neutron tests. Additionally, the project will assess the value of the ion irradiations compared to the in situ chemical and phase analysis provided by the Raman system.

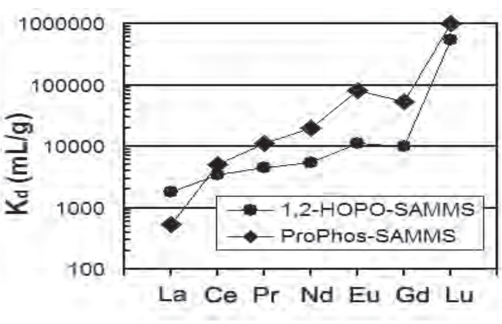
Other than demonstrating the methods, the near-term goal of this project is to identify techniques that can be used on actinide specimens for future fuel qualification acceleration. The user facilities at PNNL will be used for this work.

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 (lanthanides and transition metals) such as might be encountered in spent nuclear fuel or waste or from human blood, dialysate, high acid solutions, and natural waters. Successful development of sorbent materials for the 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 DOE site workers. ◆

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 aqueous phase. Removal of lanthanides (e.g., Ce, Pr, Gd) and transition metals (Ru, Rh, Pd) from challenging matrices (human blood, high acid solutions, dialysate, and natural waters) have not been investigated and thus will be the focus of this work. From physical and chemical properties, functional silica and both mesoporous carbon and activated carbon are evaluated in acid solutions, natural waters, and dialysate because they can withstand a wide range of solution pH (from high acid conditions up to pH 11). The small pore sizes of the materials are ideal for excluding particulates from clogging the pores, thus maintaining sorption ability. In addition to being metal collectors from natural waters and dialysate, these materials are ideal as oral drugs for limiting absorption of lanthanides and transition metals in human gastrointestinal system. For blood, functional magnetic nanoparticles are evaluated for capturing lanthanides and transition metals. The materials can be used directly in whole blood for capturing toxic species and are believed to be clinically benign.



Distribution coefficients (K_d) of lanthanides on various sorbents measured in 0.1 M HCl/NaCl (pH 2.42), initial lanthanide concentration of 50 pb (each), L/S of 5000 mL/g. The two materials have different affinity for individual lanthanides and can be used to separate them chromatographically.

During this project, six organically modified mesoporous silica (SAMMS) have been tested for capturing lanthanides (La, Ce, Pr, Nd, Eu, Gd, and Lu) in nitric acid, hydrochloric acid, river water, ground water, seawater, and dialysate against commercial activated carbon and zirconium phosphate (ZrP). Going from the acid to the alkaline side (e.g., groundwater and dialysate), the acetamide phosphonic- and diphosphonic acid-SAMMS maintain their outstanding affinity for lanthanides. Although activated carbon may have good affinity for lanthanides in natural waters having moderate alkalinity and pH, it offers small to no affinity in acidic solutions and carbonate-rich solutions like dialysate. Unlike commercial activated carbon and ZrP, 1-hydroxy-2-pyridinone (1,2-HOPO)-SAMMS is effective at removing Gd, which has recently been linked to an emerging fatal skin disease called Nephrogenic Systemic Fibrosis (NSF), and has the potential to be used in sorbent dialyzers to treat patients exposed to this lanthanide.

We have also measured the uptake capacity, selectivity, removal rate, stability, and regenerability of the SAMMS materials in relevant matrices. 1,2-HOPO-SAMMS and propionamide phosphonic acid (Prop-Phos)-SAMMS have differing affinity (K_d) for differing lanthanides, so they will be investigated for chromatographic separation of lanthanides. If we can show that lanthanide species, which are similar in charge, size, and chemistry, can be separated through this method, we should also be able to separate actinides (Am and Cm) from lanthanides using the same method. Separation of actinides from lanthanides is highly desirable because the current separation technology “TALSPEAK” requires large volume of reagents and multiple extraction steps, generating large secondary wastes and requiring high capital and operating costs.

In FY 2009, we will extend the in vitro lanthanide removal from dialysate using our novel sorbents to in vivo studies. We will create a rat model similar to patients having chronic kidney diseases whose body retains lanthanide Gd after Gd-based MRI exam that led to the development of the NSF disease in these patients. This animal model will be used to understand the mechanism of NSF disease. The goal is to develop sorbent dialysis systems for lanthanide Gd removal that will lead to NSF prevention. Sorbent dialysis systems using our novel sorbents will require less than 1 L of dialysate compared to 120 L per hour session required by a conventional hemodialysis system. These systems have potential to become personal dialysis devices that are portable and will substantially improve patients’ quality of life.

Application of Imperfection Modeling to Accelerated Fuel Clad Qualification and Characterization

Curt A. Lavender, Richard W. Davies, Dean M. Paxton, Elizabeth Z. Stephens

◆ The novel imperfection modeling approach is a statistical-based analytical method that 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 speckle pattern digital image to measure strain and describe quantitatively the sample quality, which may be used to predict future clad performance without costly and 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, by 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 advantage of this statistical distribution is a probabilistic understanding of the material performance under internal pressure conditions that can be used to predict the overall performance of a fuel cladding population, which should yield a more detailed prediction of long-term performance of a given fuel clad material.

During the first year of the project, 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 found to be indicative of the tubing quality and produced data of interest to the NRC and tubing users and manufacturers. Technically, several key outcomes occurred during the first year using the newly developed test system: 1) uniform strain was validated as much better method to evaluate tubing quality, 2) tubes were shown to have flaws demonstrated a higher imperfection level, and 3) irrespective of heat treatment, the method predicted the same level of manufactured tubing quality. FY 2008 results showed that the mechanics of material approach and data analysis were rudimentary. During the FY 2009, a more detailed analysis of the data and a more robust mechanics of material analysis will be applied.

Burst testing is commonly used to evaluate the quality of tubing; however, it only provides a single useful value of the ultimate burst pressure. Given that the burst pressure varies little with flaw content and that fuel clad tubes are homogeneous, the ultimate burst pressure varies very little. During FY 2008, the tubes typically burst at 20,000 psi with less than 200 psi variation, indicating that the tubes were of uniform quality. However, using the digital image speckle, it was found that the uniform strain varied by a factor of 8, indicating that the tube quality was variable. This result shows that the new method of evaluation can predict tube quality from a simple laboratory test like burst. It is important to understand that the variation in uniform strain is related to flaws; tubes with no flaws would have high uniform strain, and tubes with flaws would have low uniform strain. Given that the uniform strain varied from individual tubes, it can be surmised that the flaw content of the tubes was variable, although the burst pressure did not vary.

Significance of the strain variation was evaluated using an imperfection model that compares the uniform strain found in the tube to the expected uniform strain determined from the strain hardening exponent n found during a tensile test and was used to determine the imperfection value f for each tube test. The f values were then statistically analyzed using a Weibull probability plot, and a few interesting results were observed: 1) the slope of the line for all UT accepted tubes was the same, indicating that the imperfection model predicted the quality of the tube irrespective of the heat treatment condition, 2) the tubes annealed at 1080°F exhibited a more robust behavior, meaning that given equivalent flaw distribution predicted by the line slope, the 1080°F anneal rendered the tube less sensitive, and 3) tubes that were selected with UT flaws had different slope, meaning that the method can differentiate flawed from acceptable tubes.

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 to explore sensing-related applications of these materials. ◆

Nanoparticle-based biosensing and imaging have attracted considerable attention because of their potential in point-of-care disease diagnosis. We developed a biotemplated synthesis of encoded bimetallic nanoparticles for biosensing and imaging applications. The surface modification of a metal nanoparticle with biomolecules results in an increase of refraction index near the metal surface, thus providing a shift of the resonance angle. For example, gold (Au) displays a higher resonance angle shift to the change of ambient refraction index and is chemically stable. Silver (Ag) possesses a more narrow resonance curve, providing a higher signal-to-noise ratio of surface Plasmon resonance (SPR) sensors but has a poor chemical stability. Therefore, Au-Ag bimetallic nanoparticles for biosensors would contain essential advantages: they provide a high resonance angle shift to the change of ambient refraction index and narrower resonance curve, increasing the SPR sensor signal-to-noise ratio and enabling us to monitor a binding of biomolecules that could be critical for biosensing applications. In our approaches, bimetallic alloys enhance biosensor sensitivity (versus single metal nanoparticles) without loosing intrinsic device selectivity. Further improvement in biosensors may be achieved by optimizing metal composition, size, and loading of the alloy particles. The sophisticated change would generate as many different alloys as possible.

During FY 2008, we prepared Au-Ag alloys using native apoferritin as a model, consisting of a spherical protein shell surrounding an aqueous cavity of ~8 nm. Channels were generated by the multi-subunit construction of the apoferritin shell. Eight hydrophilic channels of ~4Å are 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.

The typical procedure to prepare Au-Ag alloys inside apoferritin is as follows: $AgNO_3$ and $HAuCl_4$ solutions are slowly added to aqueous horse spleen apoferritin solution, which is left overnight with stirring, dialyzed against distilled water, and then passed through a column of Sephadex G-25 equilibrated with water. Fractions collected every minute can be checked by ultraviolet absorbance at 280 nm (apoferritin). Finally, freshly prepared $NaBH_4$ solution is added to the apoferritin-containing solution to reduce the metal ion mixture to alloy. Tris-HCl and phosphate buffer cannot be used for the alloy preparation due to the silver ion that immediately precipitates; any NaCl-containing buffer also cannot be used. Therefore, distilled water and dilute urea solution (≤ 0.01 M) were chosen as reaction media.

A high-resolution transmission electron microscope (TEM) was used to characterize the structure of the alloy-apoferritin samples. The TEM images showed homogeneous particle size distributions with mean diameters of 3.2~5.7 nm. When Ag content increases, average sizes of alloys increase. It has been difficult to prepare 8.0 nm particle size alloys, which is apoferritin cavity diameter. X-ray energy dispersive spectroscopy was used to analyze the ratio of Au-Ag of the alloy products. When Ag mole fractions gradually increased in solution, Ag-Au ratios increased because the internal surface of apoferritin is negatively charged, then positively charged silver ion can occupy and reside as the $AuCl_4^-$ ion diffuses in second.

Au-Ag alloy nanoparticles within apoferritin exhibited excellent stability in solution over one month at room temperature. The addition of NaCl to reach a 0.1 M concentration did not produce precipitation. Au-Ag nanoparticles without apoferritin showed easy aggregation at a high concentration of NaCl. The apoferritin protein shell prevents the bulk aggregation of the metal alloy nanoparticles, which renders them water soluble and extremely stable.

Using nanoparticles encapsulating medical isotopes for nuclear medicine applications is new research. We have successfully synthesized $LuPO_4$/ and YPO_4/apoferritin core-shell nanoparticles based on an apoferritin protein-case template. To prepare the nanoparticle conjugates, we used non-radioactive Lu^{3+} and Y^{3+} as a model target or surrogate for medical radioactive isotope Lu-177 and Y-90. The central cavity, multi-channel structure, and chemical properties of the apoferritin protein-cage are well-suited for sequentially diffusing Lu^{3+} (or Y^{3+}) and phosphate ions into the cavity, resulting in stable core-shell nano-particles, which we characterized using TEM and x-ray photoelectron spectroscopy. We tested the pre-targeting capability of biotin-modified core-shell nanoparticles using streptavidin-modified magnetic beads and fluorescein isothiocyanate tracer. The results indicate that $LuPO_4$/ and YPO_4/apoferritin nanoparticles are promising for potential applications in radioimmuno-therapy and -imaging of cancers.

During FY 2009, we will further develop Au-Ag alloys using different protein cavities (e.g., cucumber mosaic cucumovirus, which is 29 nm in diameter and 20 nm in cavity, to produce different sizes of Au-Ag alloys). Various electrochemical and optic performances will also be investigated using the materials.

Cooperative Assembly of Active Nanomaterials and Devices

Jun Liu, Chenghong Lei, Yuehe Lin, Juan Li, Hong Wu

◆ The objective of this project is to develop new approaches to assemble spontaneous nanostructured materials and devices with integrated, desired functionalities and biomolecules. These types of materials and devices will be investigated for biotagging, molecule imaging, and other biodetection applications. Another goal is to understand the role of the active molecules in mediating the self-assembly processes. ◆

Significant progress has been made in the synthesis of a wide range of nanomaterials, but material functionalities (in particular, those derived from specialty agents and active biomolecules) are usually derived from postsynthesis treatment, procedures that greatly limit the ability to fine-tune the materials structure and properties for particular applications. For example, two specific classes of nanoparticles have been examined. Dense nanoparticles are widely investigated for molecular imaging in sensing and biodetection and for the delivery of imaging agents and drugs in disease control and treatment. Disadvantages of dense nanoparticles include the difficulty in preparation, compatibility with natural and biological environments, and lack of activity and functionality. In addition, the loading capacity, attachment, and release of the chemicals cannot be easily controlled.

We aim to develop new approaches to assemble spontaneously nanostructured materials and devices with integrated, desired functionalities and biomolecules. The materials and devices will be investigated for biotagging, drug delivery and treatment, molecule imaging, and other biodetection applications. The complex materials assembled using our approach will have the potential for novel optical coating, smart surfaces and films, antifouling, and a wide range of materials, films, and devices that demand specific chemical and biological properties. This project will also provide an ideal platform to study the role of complex molecules and biomolecules in self-assembly, which is a critical scientific challenge.

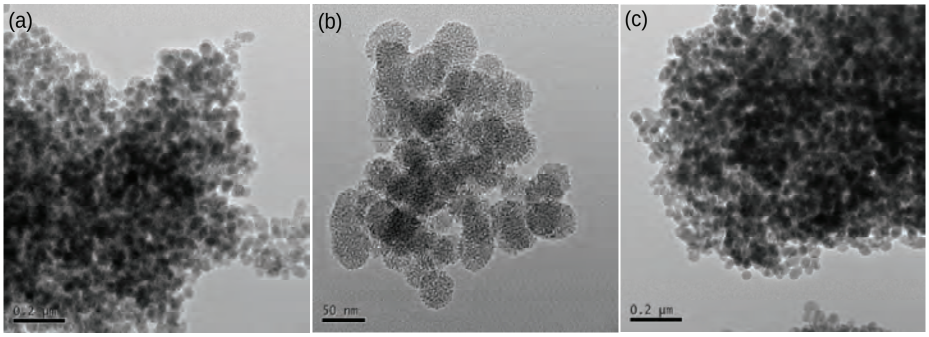
Synthesis of Functionalized Uniform Ultrafine Mesoporous Nanoparticles. Several groups reported the synthesis of mesoporous nanoparticles, which can be useful for sensing and controlled delivery. However, the preparation of functionalized, uniform mesoporous nanoparticles from 10-100 nm that can be dispersed in aqueous solutions remains a challenge. We adapted a method using triethanolamine as the pH buffer, tetraethylorthosilicate as the silica precursor, and cetyltrimethylammonium chloride as the surfactant for hydrothermal synthesis of mesoporous silica nanoparticles. After calcination, the nanoparticles were further functionalized with aminopropyltriethoxysilane, followed by reaction with salicylamide and other agents. We demonstrated that uniform mesoporous nanoparticles can be obtained and redispersed in appropriate aqueous solutions.

Entrapping Hydrogenase Enzymes in Functionalized Nanoporous Materials. First discovered in the 1930s, hydrogenase enzymes play a vital role in anaerobic metabolism. Hydrogenase is an enzyme that catalyses the production of hydrogen or the reversible oxidation of hydrogen, and is therefore very important for hydrogen production for DOE's hydrogen initiative. Currently, maintaining the stability of the enzyme is a critical problem.

Hydrogenases are mainly classified according to the metals thought to be at their active sites: iron (Fe)-only and nickel-iron hydrogenase. The Fe-only hydrogenase is more active but more oxygen-sensitive (i.e., much more unstable in the presence of oxygen). Recent advances in our lab using functionalized mesoporous silica (FMS) provide an innovative approach for entrapping enzymes electrostatically in HOOC- or NH_2- FMS. This approach may not only enhance the enzyme activity, but also the high local concentration of the formed "electrostatic salt" may be able to make the oxygen salt and accordingly enhance the oxygen tolerance of the enzyme.

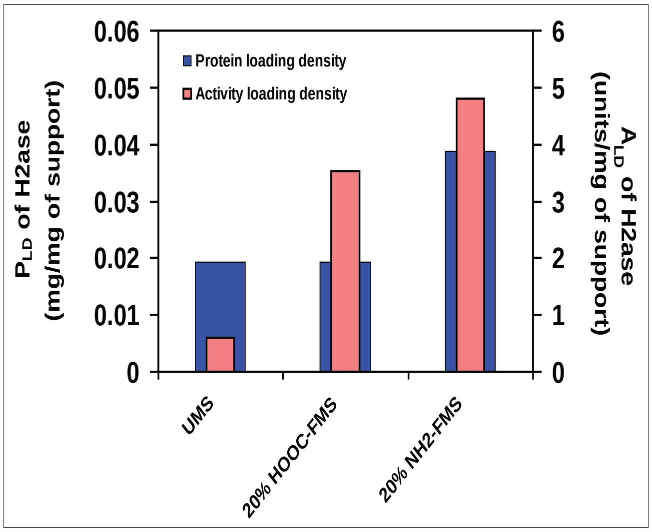
For this project, we worked with the Fe-only hydrogenase from two bacterial strains, *Desulfovibrio desulfuricans* and *Clostridium pasteurianum*. We entrapped both the purified enzyme and the bacterial cell lysate in a variety of functional porous materials (including FMS) and compared these with the free hydrogenase activity in solution.

Bacterial Cell Fermentation and Cell Lysis. Desulfovibrio desulfuricans spp. *aestuarii* (ATCC 29578) and



TEM images of uniform mesoporous silia nanoparticles: a) calcined mesoporous silica nanoparticles before functionalization, b) mesoporous structures in calcined mesoporous silica nanoparticles before functionalization, and c) mesoporous silica after functionalization.

Clostridium pasteurianum (ATCC 6013) were anaerobically cultured in ATCC medium 1250 and 1053, respectively, at 20-30°C. We grew the cell culture in a large carboy (~10 L) bubbling with N_2 to keep them anaerobic in ATCC mediums. We were able to harvest ~10-30 g of cell per 10 L of the cell culture by centrifugation at 10000 g for 1 h at –4°C. The cell pastes were stored at –80°C when not in use. The bacterial cells were suspended in a lysis buffer containing pH 8.5, 100 mM TRIS-HCl, and lysed two times using French Press for purification at 4°C.



Enhanced enzyme activity by immobilization in mesoporous silica and comparison of the activity of the hydrogenase from Clostridium pasteurianum entrapped in FMS. The specific activity of the enzyme stock solution was 132.1 units/mg, while the specific activity of the enzyme in 20% HOOC-FMS was 182.0 units/mg.

Immobilization of the Hydrogenase and Cell Lysate and the Enzymatic Activity Evaluation. We set up a glovebox for the experimental operation and used functionalized (30 nm 20% NH_2- or HOOC- FMS) and unfunctionalized mesoporous silica (UMS). We also tested the larger porous materials (pore size above 50 nm), the strong cation and anion exchange media (Poros 20HQ and 20HS) based on the coated polystyrenes. The incubation solution in the absence of the nanoporous materials was used as a control. We established a fast, convenient spectrophotometric method to evaluate the free and immobilized hydrogenase activity. We added the enzyme sample in a standard cuvette containing 0.14 mM methyl viologen reduced by sodium dithionite in the degassed pH 8.0, 50 mM TRIS-H_3PO_4. The kinetic change of absorbance of methyl viologen at 600 nm was recorded during H_2 evolution. We observed that the hydrogenase activity is greatly enhanced in the solid supporting materials. However, in all our experiments of the hydrogenases from two bacterial strains with two series of functional porous materials thus far, the extreme oxygen sensitivity of the hydrogenase has yet to be overcome. Further experiments with much higher coverage of electrostatic functional groups should be tested.

Development and Understanding of Nanostructured Materials for Advanced Energy Storage

Z. Gary Yang, Jason Zhang, Kevin M. Rosso, Jian Zhi Hu, Li-Qiong Wang, Daiwon Choi, Donghai Wang, Guan-Guang Xia, Leonard S. Fifield, Chongmin Wang, Larry R. Pederson, Gordon L. Graff, Jun Liu

◆ Fundamental improvements to electrochemical storage performance are essential for emerging applications, particularly in the transportation and electricity production sectors. ◆

Energy security and environmental concerns have spurred significant interest in developing advanced energy storage technologies for emerging applications such as plug-in hybrid vehicles or the efficient use of renewable energies. In particular, batteries and supercapacitors have been identified as critical enabling technologies to accomplish DOE's strategic goal of protecting "our national and economic security by promoting a diverse supply and delivery of reliable, affordable, and environmentally sound energy." Although they have gained commercial success for mobile electric applications, batteries such as lithium (Li)-ion fall short of satisfying the requirements for the emerging, large-scale applications in terms of energy/power density, life, safety, and cost.

Given that the performance of electrochemical storage devices ultimately depends on the properties of the electrode and electrolyte materials, the emerging applications require revolutionary breakthroughs in the electrochemically active materials. In particular, next-generation energy storage materials must have a greatly improved charge transport and electrode kinetics while maintaining structural and interfacial stability, enable high voltage and multi-electrons per redox center for high-energy density, and meet rigorous cost requirements. One group of materials that potentially satisfies the stringent material requirements are nanomaterials, which may offer multiple advantages, including improved structural and mechanical stability (thus longer cycle life), enable new reactions not possible in bulk materials, leading to a higher energy, and short electron/ion transport distance and higher charge/discharge rate, permitting a higher power. The size reduction, however, may be accompanied with potential disadvantages, such as side-reactions that may negatively affect the performance of energy storage devices. To use the advantages and avoid the potential disadvantages for the energy storage applications to their fullest capability, nanomaterials may require synthesis routes that not only control size but also desirable crystallinity, morphology, and possibly multi-function surfaces.

There is a lack of fundamental understanding of nanostructure effects on performance in energy storage materials and a serious lack of viable high-volume, low-cost manufacturing routes for nanostructured components, both of which would help design and develop optimized nanostructures for electrochemical energy storage applications. Thus, there is a pressing need to gain a mechanistic understanding of the effects of size/interfaces on electron/ion transport, electrode reactions, and charge storage at the nanoscale and develop economic synthetic approaches that enable cost-effective production of nanostructures with desirable features for energy storage applications.

In FY 2008, our research efforts focused on understanding the charge transport in nanostructured materials and initial synthesis/assembly of anode, cathode, and electrolyte/cathode interface nanomaterials for Li-ion batteries. Low temperature approaches, including template-assisted and 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 NMR and transmission electron microscopy (TEM), electrochemical studies were performed to understand fundamental charge transport in the electrochemically active materials and the effect of processing/nanostructure on charge transport/separation. We also initiated the computer modeling effort to understand and predict the nanosize effects on electron/Li+ (ion) transport in the synthesized nanostructures. Modeling efforts established a computational framework that can be fully extended and deployed in successive years.

Materials Development. Silicon (Si) has one of the highest theoretical specific capacities (4200 mAh/g) among potential anode materials used in Li-ion batteries, but its practical applications have been limited by the large volume expansion (~300%) associated with Li intercalation. In an attempt to maintain structural integrity, several groups have investigated the electrochemical performance of Si NWs. However, the methods used by Sanyo (sputtering) and the Stanford group (vapor-liquid-solid reaction) are not appropriate for large-scale applications due to their high cost and/or use of toxic precursors. In addition, the true capacity of the anodes (including substrate) is also much smaller than those calculated using only the mass of the Si nanowires. We developed an approach for large-scale preparation of the Si nanowire-based anode by high temperature synthesis. Free-standing Si nanowires have been grown from commercial bulk silicon powders without substrates and toxic precursors. In our process, all precursors in a container are simultaneously converted to Si nanowires, and growth is not limited to a substrate surface. Therefore, they can be easily modified for large-scale production.

Ultimately, the diameter of nanowires varied from 30 to 200 nm. Si-based nanowires have been characterized by various methods, including X-ray diffraction, scanning electron microscopy (SEM), and TEM. The detailed chemical and structural analysis indicates that the composition of the nanowire strongly depends on the sample preparation conditions. The high-temperature synthesized Si nanowires often contain oxygen (SiO_x; due to oxygen contamination) or SiC (if synthesized in a furnace with a carbon liner).

Electrochemical properties of these nanowires have been measured. The initial capacity of the nanowires is approximately 1500 mAh/g, but they still exhibit a significant capacity fade due to contaminations. In an alternative approach, Si nanowires were etched from either Si wafers or powder in aqueous solutions of 0.02 M $AgNO_3$ and 5 M HF for 16 hours. The etched Si wafer was washed several times using water. Excess Ag was removed in a nitric acid bath for at least 1 hour, followed by water washing. The SEM micrograph indicates that the length of Si NWs is ~30-40 µm and the diameter is approximately 200-500 nm. Additional work needs to be executed to improve the performance of the Si nanowire-based anode, which includes further reduction of the synthesis temperature to minimize formation of SiO_x, post-treatment of the nanowire to reduce SiO_x to silicon, and further development of the chemical-etching method for the production of Si nanowires.

As potential anode material for Li-ion batteries, TiO_2 is limited by sluggish Li and electron transport kinetics. To improve its Li intercalation activities, we developed a low-temperature solution approach that is capable of making highly crystalline mesoporous TiO_2 with a tunable pore size in few nanometers. The mesoporous rutile was built upon blocks of nanorods that were interconnected and aligned along c [001] directions. The increased surface area (245~300 m^2g^{-1}) and shortened Li distance (particularly in ab planes) led to substantially improved Li-intercalation properties. The mesoporous TiO_2 synthesized with a pore size of ~2.0 nm enabled to accommodate Li up to $Li_{0.7}TiO_2$ at the first discharge at 0.4 mA/g (C/5) and 1~3.0 V vs. Li^+/Li, of which 0.55 mol of Li per mol TiO_2 ($Li_{0.55}TiO_2$, 185 mAh/g) was able to be cycled reversibly. Upon Li-intercalation, the rutile structure was irreversibly transformed into $LiTiO_2$, and the mesoporous nanostructures remained stable over the Li-intercation/deintercalation cycles. Thus, the rutile mesoporous nanomaterials demonstrated a remarkable capacity retention, averaging only 0.x% capacity loss during the first 100 cycles, along with a much improved rate capability.

Modeling. The molecular modeling aspect of this project had the overarching objective of providing the theory support and fundamental understanding in the dynamics of coupled charge and ion transport in metal oxide electrodes under development for energy storage. The modeling effort is focused on the multiscale problem of simulating the collective diffusivities of ions and charge-compensating e/h^+ carriers in single-crystal particles across grain boundaries and through networks of grains for select systems.

During FY 2008, we performed simulations aimed at determining the mobilities of coupled electron and Li^+ ion transport in polymorphs of TiO_2 using primarily molecular dynamics simulations. As part of this effort, we also 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 Li^+ ion content. Two manuscripts are in development. The modeling effort will be expanded during FY 2009 that increases our momentum in this topical area.

NMR Study. We have applied hyperpolarized (HP) ^{129}Xe NMR for the first time to obtain information on the porosity and interconnectivity of pores for highly crystalline mesoporous TiO_2, a promising anode electrode material. In this work, it has been shown that HP ^{129}Xe NMR measurements allow differentiation between similar-sized pores within different crystalline phases. Both anatase and rutile pores of 4 nm size were identified in mesoporous TiO_2. The values of the heat of adsorption for anatase and rutile pores are 9.8 and 14.2 kJ/mol, respectively. In contrast to other pore characterization methods (such as Brunauer-Emmett-Teller), we were also able to probe interconnectivity between pores constrained to different phases. The cross peaks in two-dimensional exchange (exchange spectroscopy) NMR spectra show that exchange takes place between both types of pores and the free gas with a short mixing time of 5 ms, indicating that these two types of pores are well interconnected. Such information on porosity and interconnectivity is critical for understanding the likes of Li-ion transport mechanisms in mesoporous TiO_2 anode materials.

Successful completion of this research will lead to a fundamental knowledge of the role of nanostructures in electrochemical energy storage, a scientific understanding of processing routes necessary to produce desirable structures, and breakthrough materials and chemistries with improved charge transport, electrode kinetics, structural and interfacial stability, higher energy density (through higher operating voltage and/or multi-electrons per redox center), and cost-effective routes to manufacturing.

Fate and Transport of Titanium Dioxide Through Freshwater Ecosystems

Ann L. Miracle, Amoret L. Bunn, Daniel J. Gaspar, Jeffrey A. Ward

◆ This project has provided fundamental information about the measurement and fate of nano-sized TiO_2 with various compartments that would make up a freshwater ecosystem. The ability of nanoparticles to aggregate in different environmental media, bind to environmental materials, become bioavailable, or initiate physiological effects remains areas of research with little current data. Resolution of even some of these parameters will be critical to assess the potential risk for environmental and ultimately human health. ◆

The environmental fate and transport of nanoscale titanium dioxide (titania, TiO_2) or any nanomaterials entering dynamic aquatic environments have never been studied in a quantified manner. Because nanoscale TiO_2 properties are dependent on size, surface chemistry, and composition, the movement, toxicity, and bioaccumulation of these materials are difficult to study in a complex ecosystem. Titania materials are likely to enter an aquatic environment through wastewater treatment plants or directly into recreational waters. Because these materials are durable and recalcitrant, the accumulation of nanoscale TiO_2 in the environment could be significant over time and cause unforeseen impacts on ecosystems. Research that demonstrates the capability to characterize and quantify nanoscale TiO_2 distribution in different environmental compartments (i.e., water, sediment, and biota) will be relevant to setting guidelines for risk analysis.

A material of nanoparticle size does not necessarily possess the same fate and transport, exposure, and effect characteristics of that same material at the micro- and macroparticle size. Although there have been studies that demonstrate the difference in dosimetry and exposure of nanoparticles, relevant environmental conditions that may alter the chemistry and composition of the nanomaterials are often not considered. This project focused on identifying and quantifying TiO_2 nanoparticles and the subsequent mass balance of TiO_2 in environmental media in order to determine the likely fate and transport of metal nanoparticles in a freshwater environments.

Two different types of TiO_2 were used for fate and transport experiments: pure anatase, 5-30 nm in water dispersion and an anatase/rutile mixture, less than 75 nm in water dispersion. Dispersion and size were confirmed using scanning electron microscopy. The titania solutions were added to separate triplicate mesocosms with continual 50 mL/min flow rate of Columbia River water (CRW) at a concentration of 5 ppm for 12 hrs, followed by an additional 36 hrs of unamended CRW at the same flow rate. Water samples of the dosing solution, inlet, and outlet of the mesocosms were collected prior to titania addition and at 1, 8, 12, 13, 24, 36, and 48 hrs post-titania addition for TiO_2 mass analysis.

Mesocosms were constructed using sterile Accusand at 2 cm deep sediment in 15 x 15 cm mesh baskets, which were placed in chambers designed for flow-through aquatic exposures. Flow rate was regulated by peristaltic pumps. Six Asiatic clams (*Corbicula fluminea*) and 25 amphipods (*Hyallela azteca*) were added to each of the nine total mesocosms to provide three replicates per treatment (two forms of titania and control). Biota and sediment samples were collected following the conclusion of the 48-hr exposure and analyzed for TiO_2 uptake.

For both nanomaterials, there were visible flocs throughout the dosing portion of the experiment. The material was observed to settle out over the sediment, thus accounting for the rapid loss of titania from the inlet to the outlet of the mesocosms. The sediment analysis indicated that indeed the majority of sediment-associated titania was present in the inlet third, with a gradient in decreasing concentration for the middle and outlet thirds. However, more of the anatase titania nanomaterial solution was associated with the sediment (0.5%) than the anatase/rutile titania nanomaterial (0.08%).

A greater percentage of anatase titania was associated with the amphipods (48 mg/g) than the clams (0.55 mg/g). This difference was visible in that the amphipods appeared coated with the nanomaterials, while the clams were observed to flush out visible titania flocs through their excurrent siphons and through deposition in fecal material. Although the same observations were also made with the anatase/rutile exposures, a greater concentration of titania nanomaterial was associated with amphipods (67.8 mg/g) and clams (1.2 mg/g). Inductively coupled plasma optical emissions spectroscopy was used to assess a mass of TiO_2 associated within a matrix. The experimental data generated from all compartments was used to parameterize and validate a physically based process model from the conservation of mass for each phase (i.e., water, sediment, biota).

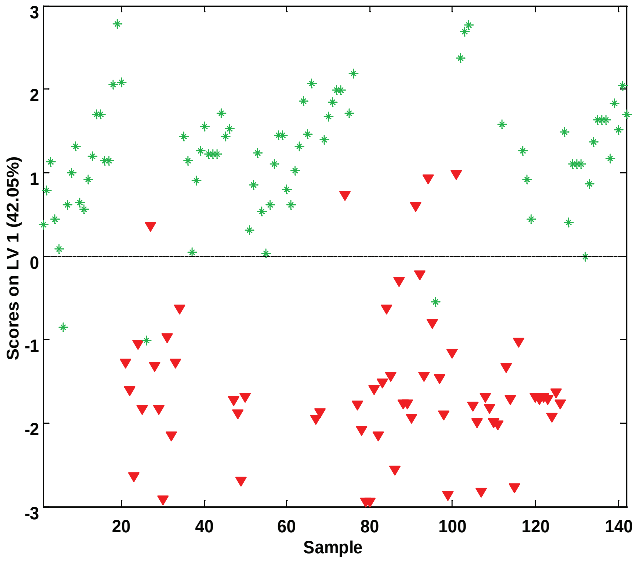
Information-Driven Discovery of Radiation Detection Materials

Kim F. Ferris, Bobbie-Jo M. Webb-Robertson

◆ The fundamental connection between the performance of radiation detectors and underlying physics of detection materials is explored by extracting knowledge in collections of radiation-detection materials data. This knowledge is used as a basis for generating "virtual" materials candidates and estimating their physical properties from a behavioral viewpoint. The combination of these "virtual" materials with the multiple physical property requirements allows us to assess the viability of these materials prior to synthesis. ◆

Radiation and nuclear materials pose a potentially dangerous threat for terrorist activities, yet methods to detect such materials are 30 years old and falling behind current needs. Unfortunately, the current material synthesis/characterization/development process used to identify detection materials is costly and time intensive, making it impractical to explore more than a few materials at a time. PNNL is using its expertise in materials informatics to narrow candidate materials for development and speed the discovery of materials with a greater chance of success in detecting radiological and nuclear materials before they are used against our nation.

The identification of a new composition or materials class that meets the multiple physical property requirements for radiation detection faces the daunting problem of numbers: even for a simple binary system, A_mB_n; m,n=1-3, the number of potential candidate materials is over 300,000. Traditional approaches to materials development tend to rely on a data point-by-data point approach and quickly become highly dependent on prior art and variations of current topical materials. More importantly, the number of new candidate materials that can be developed from a laboratory-intensive approach is small and limited by the investigator's synthetic expertise, especially compared with the potential number of elemental combinations.



Efficient information-based classification (over 95%) of materials into electronic classes using composition based criteria: semi-conductor (lower) and scintillator (upper).

Researchers at PNNL have used a materials informatics approach to create a framework for an information-based learning process that uses the collective power of materials information to achieve greater efficiency in exploration. The knowledge development process results in the identification and ranking of viability of potential materials, design guidance for synthetic efforts, and metrics for performance limits of materials classes. Model- and design-centric approaches are systematically explored using a variety of techniques to assess robustness and interrogated to generate virtual candidates, which are computationally constituted materials that may or may not have been synthesized and fully characterized experimentally.

The primary objective of this project is to develop a method that allows us to identify new materials more quickly, satisfying requirements for radiation detectors from the large number of potential candidate materials. To accomplish this goal, our project focused on two aspects: information-based strategies to down-select large populations of "virtual" candidates to the select few satisfying the radiation detector performance requirements and a mechanistic structure for science-based discovery of new materials, transforming individual collections of data into group knowledge.

During FY 2008, the project focused capabilities to semiconducting radiation-detection materials. The first technical target was prediction of band gap energies for "virtual" candidate materials based upon the material's composition in the absence of a crystal structure determination. As shown in the figure, materials informatics results in a highly efficient categorization (95+%) of candidate materials into semiconductor and scintillator (insulator) classes. Model optimization within these materials classes results in band gap predictions with accuracies consistent with first principles electronic structure computations. This informatics model enables a whole new area of materials development, removing the expensive constraint of materials synthesis in the early stages of materials selection. Extensions to this new materials approach have led to strategies for the development for lightweight alloys and medical imaging materials. This research has also led to PNNL capabilities in the emerging field of materials informatics for materials research, resulting in a number of invited publications and presentations.

Ion Beam-Nanoparticle Interactions for Radiation Detection

Marvin G. Warner, Jay W. Grate

◆ The work performed under 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. These semiconductor nanoparticles, called quantum dots, 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 nanoparticle and prevent aggregation. While the photoluminescence properties of quantum dots, which depend intimately on parameters such as size, shape, and composition, are relatively well-understood in the open literature, research on the radioluminescence response of these materials 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 the well-characterized photoluminescence properties of the materials and by extension their composition and structure, with the radioluminescence responses observed upon exposure to ionizing radiation.

If a correlation exists between photoluminescence and radioluminescence responses, then the first predictive understanding of the radiation physics of quantum dots will be developed. Further, an understanding of how photoluminescence properties correlate to radioluminescence responses allow us to synthesize new materials for radioluminescence applications designed *a priori* to possess specific radioluminescence characteristics. However, if there is no direct correlation, these studies will represent some of the first measurements of the interaction of energetic ions with quantum dots, determining their potential as materials for the detection of ionizing radiation and providing insight into the effects of chemical composition and structure on the radioluminescence properties. Moreover, systematic studies will help understand the scintillation mechanisms, where photoluminescence includes 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 proposed to understand the correlation of the photoluminescence and radioluminescence properties of a variety of nanostructured materials through an integrated program of research, including quantum dots synthesis and characterization as well as physical measurements. During FY 2008, we performed a directed investigation of how quantum dots composition, shell structure, surface modifications, and local environment (capping layers and composite matrixes) influence their photoluminescence and radioluminescence properties, measuring such parameters as fluorescence quantum yield (light yield), ion-induced luminescence spectra, resolution, and decay time. Specifically, 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 that have been adapted in our laboratory for these studies.

Once materials were synthesized and purified, thin films were formed on quartz substrates for analysis using the ion-beam system. Prior to ion-beam analysis, the thin films were characterized using a variety of techniques, including scanning electron microscopy, scanned probe microscopy, and optical profilometry that were employed to determine the morphology and quality of the films formed using two different methods (drop casting and spin coating). Both drop cast and spin coated films were tested in the ion-beam apparatus, and it was discovered that the higher quality (i.e., more homogenous) thin films produced using the spin coating method led to better radioluminescence response. We made several modifications to the ion-beam system that enabled us to make unique measurements of nanostructured thin films.

In FY 2009, we will continue developing new quantum dots materials, measuring both their photoluminescence and radioluminescence properties to correlate how changes in structure and functionality affect observable properties.

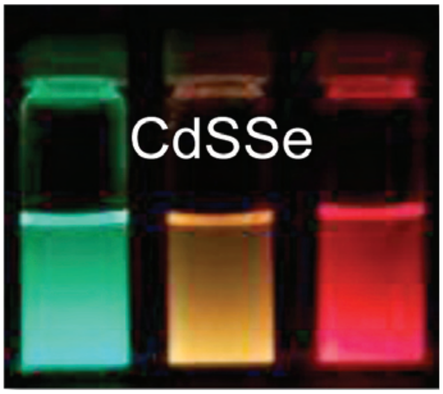


Image showing three different quantum dots with different emission wavelengths synthesized under this project.

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 found 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 of this project is to establish a laboratory-based experimental method to measure leak rates reliably in prototypic through-wall stress corrosion cracks. ◆

Leak-before-break is a design methodology critical to ensuring the safe use of piping components in light water reactor systems. During the past few years, leak-before-break has received increasing applications for assessing and upgrading the safety of existing nuclear power plants against guillotine-type breaks. Several models exist, but limitations exist in the leak rate database that underpin these models. The shortcomings include unrealistic crack morphologies, uncertainties in weld residual stresses, and no knowledge of leak rates through tight, partially oxide-filled stress-corrosion cracks common to most current leak-before-break concerns. 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 first, it is necessary for the utility companies to install massive pipe restraints and shielding at a great cost. The DOE and governmental regulating bodies are strongly involved in the development and use of this criterion to ensure that it is implemented accurately and correctly. Thus, there is significant interest both from the U.S. government and the utility companies in determining whether piping systems will leak before breaking.

This research will develop and demonstrate an approach to measure quantitatively leak rates reliably. 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. Existing equipment is being slightly modified so that it is capable of growing a crack into a specimen and measuring the leak rate through the crack when it has reached a predetermined length. The main goals will be to assemble a unique test system and produce essential leak rate data for prototypic cracks in light water reactor structures for the first time. This activity will demonstrate unique potential for this approach and strengthen PNNL's ability to address critical materials reliability issues in nuclear power systems.

When the leak-before-break analysis method began 25-30 years ago, fatigue type cracks were thought to be the only type of cracks that would form in these piping systems. In recent years, it has become apparent that stress corrosion cracking occurs and is far more prevalent than fatigue cracking. The leak-before-break analysis method is undergoing revision to predict leak or break for stress corrosion cracks. One aspect of this method that is in strong need of development is a technique to assess leak rates accurately in through-wall stress corrosion cracks. Current methods for measuring leak rates in fatigue cracks are not suitable for measuring the same in stress corrosion cracks. Technology needed to perform leak rate measurements through real intergranular stress-corrosion cracks will be developed, establishing a unique new capability to generate essential data needed to establish reliable leak-before-break models for stress corrosion cracks. These models are needed to assess light water reactor piping conditions and to aid in the further development of leak-before-break component design methodology. The leak rate capability will be shakedown tested by measuring leak rates through stress-corrosion cracks created under simulated pressurized water reactor conditions.

This project started in the final quarter of FY 2008 with limited funding for work, which focused on modifying laboratory equipment to allow leak rate measurements and also to prepare a fatigue-cracked specimen to test the initial equipment modifications. Both tasks were accomplished, with the stage now set to test the initial modifications in early FY 2009 work, which will continue with the proposal-developed work plan. After the initial changes are tested, further modifications will be made to the equipment as needed to improve the leak rate measurement technique so that it can be used to study a wide range of stress corrosion crack morphologies. Stress corrosion crack specimens will also be prepared in FY 2009, with testing of these specimens taking place in late FY 2009 and early FY 2010.

Measurement and Modeling of Slag Critical Viscosity, Optimization of Slag Chemistry, and Refractory Degradation in Coal Gasifiers

S. K. Sundaram, Siva P. Pilli, Kenneth J. Johnson, Rick E. Williford, Josef Matyas, Scott K. Cooley,
John S. Mccloy, Jarrod V. Crum, Autumn B. Edmondson, Sara C. Longanbach (Michigan State University)

◆ The conversion of coal into clean-burning liquid fuel shows significant promise from economic, environmental, and security perspectives. This promise of gasification technologies for solid feedstocks will be realized through durability of refractory materials. ◆

Development and improvement of refractory systems tops the list of 20 research and development needs ranked by frequency of identification. The development of advanced gasifier performance models and the characterization of coal slag and ash were also listed within the top 10 needs. According to the Vision 21 Technology Roadmap, the performance objectives are to achieve 3 to 4 years of refractory life, develop materials that can be recycled without hazardous waste disposal, and optimize thermal properties (the current life of gasifier refractories is 12 to 16 months and that of combustors). In spite of continued research in this and other gasifier areas, most power plants do not use the best materials. Additionally, optimum materials are not currently available to meet Vision 21 plant needs. High temperature (1300–1600°C), large and sudden temperature variations and thermal stresses, alternating oxidizing and reducing conditions, high pressure, corrosive slag, and erosive residual particulates make the gasifier environment extremely challenging. The state-of-the-art clearly shows that the refractory performance remains a critical issue, and there is still a need to develop better refractory materials for this industry. The overall objective of this project 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 and also to validate the model experimentally.

Since FY 2006, we have made significant progress in every aspect of the project. Select results are summarized below:

- We integrated 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.
- Refractory degradation submodel was ready for expansion. Slag flow submodel was tested with our experimental dataset. Two refractory physical spalling models were completed.
- We used statistical models to design a slag chemistry test matrix that will cover U.S. coal slag chemistries. We prepared and characterized 20 test slags in our laboratory and measured slag viscosities and critical viscosities of select slags in air atmosphere. An extensive study of refractory-slag interaction was completed, and experimentally measured slag penetration depth in air was inputted into the refractory degradation model. The experimental viscoelastic properties of select slags in air have also been inputted into the slag flow model.

Our progress during FY 2008 is summarized below.

- A refractory degradation submodel was applied to predict the failure region and modes using the experimental slag penetration data. The slag flow submodel was modified to represent hot-wall gasifier and tested with our experimental dataset. A third refractory spalling model on a composite diffusion coefficient that connects the physical processes and refractory chemistry was completed.
- The refractory-slag interaction in reducing atmosphere study was studied. 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. We also developed chemical and electrochemical schemes to protect refractory.
- An American Association for Advancement of Science annual meeting symposium was organized in February. Other presentations included an invited poster at the 7th Symposium on High Temperature Corrosion and Protection of Materials and eight presentations at Pittsburgh Coal Conference. A total of five research papers were published.

In FY 2009, we will continue with final validation of all models. We plan to use an integrated model for operation of the research gasifier in PNNL and demonstrate the slag chemistry/refractory degradation models and refractory protection schemes in the gasifier.

Micro-Structured and Membrane Reactors for Intensification of Multiphase Biomass Conversion Process

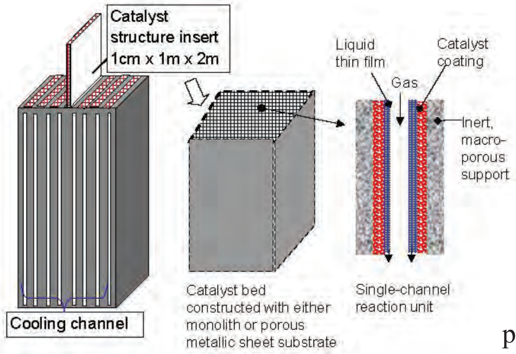
Wei Liu, Doug Elliot

◆ This project aims to develop innovative reactor design ideas that enable energy-efficient and compact chemical processing plants for biomass conversion. Successful results from this project will open new opportunities in the catalyst and reactor technology areas for the biomass conversion process and enable transfer of the laboratory results into practical impacts. ◆

This project aims to build strong reaction engineering research capabilities at PNNL for multiphase catalytic reactions in biomass conversions. Cost reductions for biomass conversion plants are critical to ensuring biomass is a viable resource for fuel and chemical production in lieu of petroleum. Research efforts in this area have been devoted to catalyst preparation, characterization, and reaction chemistry. Present technical approaches attempt to integrate catalysis and materials processing with reactor designs, and to come up with process technology concepts for dramatic improvement to the process performance.

Particle-based slurry and packed beds are commonly used to conduct multiphase catalytic reactions in the industry and in laboratories. Conventional reactor technologies are often associated with problems and limitations in hydrodynamics, mass transfer, catalyst leaching or attrition, and scale-up. The problems become significant with the biomass-related reaction process, where hydrogen or oxygen gaseous molecules have low solubility in the water solution so that the reaction often becomes limited by mass transfer of gaseous reactant or product into or out of the catalyst pore. For example, hydrogenation of glucose to sorbitol is limited by hydrogen mass transfer in slurry or trickle beds.

A solid catalyst (Ru/TiO_2) was discovered at PNNL for this reaction with excellent stability and selectivity. Glucose conversion monotonically decreases with lowering reactor pressure. At the same reactor pressure, glucose conversion increases with feed H_2/glucose ratio. This work suggested that high reactor pressure and high H_2/feed ratio are needed to achieve high throughput with the particle packed bed reactor. However, the high reactor pressure and high H_2/oil ratio result in high capital and operation costs. Issues with slurry bed reactors for this reaction process has been noted where catalyst leaching into the product solution becomes a serious problem in addition to the high-pressure reactor operation.



The reactor is engineered at three scales to address intrinsic mass and heat transfer in a single reaction unit, flow distribution, and heat conduction among different channels as well as heat transfer between the catalyst bed and environment.

For recent years, micro- and mini-structured catalyst bed and reactor concepts have been proposed and studied for multiphase catalytic reaction processes. Among micro-structured beds made of different materials (glass, steel, ceramics, etc.), ceramic honeycomb-based structures are preferred in this work because of thermal and chemical stability, and demonstrated manufacturability and cost in catalytic converters, diesel filters and membrane filters. Furthermore, the porous matrix structure of the ceramic monolith body enables good catalyst adhesion and different reactor configuration designs.

This project focuses on multiphase catalytic reactions because they are commonly used in the biomass conversion process. The multiphase reaction is often limited by mass and heat transfer and hydrodynamics, and the conventional reactor technologies are associated with strong-scale economy.

We made significant progress during FY 2008 in making structured catalyst beds that are not currently available. Project milestones include the following:

- We identified a coating formulation and application process to deposit catalysts on porous channel walls of a ceramic honeycomb support, which is a prerequisite for desired performance attributes.
- Porous, thin metallic substrate sheets were fabricated and evaluated for deposition of catalyst and/or membrane materials of different pore sizes. This provides a material platform to build micro-channel membrane reactors.
- Prototypes of a new reactor structure that allows close integration of reaction with heat transfer and better use of catalyst were made. The reactor assembly and shake-up testing was conducted with Fisher-Tropesch reaction.

The success of the present project will open up a new opportunity in the catalyst and reactor technologies for the multiphase reactions in the biomass conversion process. The process capacity for biomass conversion plants is much smaller than oil refineries and petrochemical plants. By intensifying multiphase reaction processes at all scales of the reactor design dimensions (catalyst, coating and channel, bed), a process pipeline-like reactor unit may be developed.

Modeling Nonlinearity in Inorganic Scintillators and Semiconductors

Kevin M. Rosso

◆ This project has deepened our understanding of spectroscopic nonlinearity in radiation-detection crystals and enhanced our ability to discover next-generation materials. It has provided a basis for design principles that permits more linear, high-resolution detector response with the aim toward improved detection and prevention of the proliferation of nuclear and other weapons of mass destruction. ◆

Gamma-ray detectors are widely used in the interdiction of special nuclear materials smuggling and in the prevention of nuclear weapons proliferation. Understanding spectral nonlinearity is part of a broader effort to decipher the basic condensed matter physics of radiation-detector materials and devices. Improved linearity in radiation detectors will permit more accurate measurements of gamma-ray and particle energies, which will in turn permit more accurate identification of radioactive isotopes or nuclear reactions, including by remote or noninvasive sensing. In addition, there are potential applications in medical imaging, astrophysics, high-energy and nuclear physics, environmental monitoring, and oil exploration.

This theoretical/computational project had the overarching objective to determine the causes and magnitude of energy nonlinearity in radiation spectrometer materials. To do this, we used kinetic Monte Carlo (KMC) simulation to construct a numerical computational model of the energy transfer process in alkali halide scintillator materials. This model has allowed us to assess the energy dependence of elementary relaxation processes and transport and the recombination of excited carriers as a possible explanation for nonlinearity. The effects of trapping and radiative versus nonradiative recombination at activators and native defects are important and were explicitly incorporated. A fundamental picture of the causes of nonlinearity has emerged for two inorganic scintillators, and this insight will aid in the development of new more linear detector materials.

We designed and implemented a KMC program based on the three-process model first introduced by Dietrich and Murray, which previously was used successfully to fit scintillation decay curves of NaI(Tl) and CsI(Tl). In this model, three energy-transfer processes are responsible for scintillation: 1) the capture of electrons and holes at activator sites, followed by radiative decay of the excited activators, 2) the capture of electrons at activator sites, followed by diffusion of holes to those sites and radiative decay of the excited activators, and 3) the capture of electrons and holes at separate activator sites. The electrons are then thermally released and captured at activator sites that have trapped holes, and radiative decay of the excited activators follows. We focused on the alkali halide compound CsI both pure and doped with a range of thallium concentrations. The KMC model used an explicit atomistic representation of the crystal lattice, activator sites, defect sites, and individual electron-hole pairs. The probability of individual diffusion, recombination, and scintillation events was calculated from rate equations parameterized with data published in the literature. The concept was to prove that the model needs only a selection of rate constants for key processes to reproduce the experimental behavior. The prediction of rate constants from first principles would therefore eliminate the dependence of the model on experiment for making linearity predictions, making this the first non-phenomenological theory tool for detector materials design.

Using the decay constants derived experimentally and spatial distributions of e/h pairs calculated using NWEGRIM, the KMC model reproduced the scintillation decay curves of CsI(Tl) for several activator concentrations. The simulations also worked well for $LaBr_3$(Ce). Scintillation decay curves, relative intensities of emission peaks, and light yields were computed and found to be in good agreement with experimental data for a range of temperatures and activator concentrations. This demonstrated that the KMC scintillation model is capable of reproducing both the kinetics and efficiency of the scintillation process in two inorganic scintillators having relatively extreme observed linearities in light output. In addition, novel predictions emerged from our simulations, such as the diffusion distance distributions of self-trapped holes and excitons. When combined with NWEGRIM, the resulting KMC scintillation model provides a rigorous framework for "thought experiments" to probe possible physical processes responsible for the nonlinear relationship between scintillation light yield and incident gamma-ray energy.

To extend the applicability of the model to other materials where rate constants for elementary processes are less well documented, any future work would entail the increased use of ab initio electronic structure calculations to predict activation barriers for electron and hole transport, the transport of self-trapped excitons, and radiative and non-radiative decay processes. Such calculations in principle should be able to reproduce correctly the rates of key energy transfer processes for scintillation.

During FY 2008, this project yielded two journal articles summarizing our novel approach and the theory-experiment agreement for CsI(Tl) and $LaBr_3$(Ce).

Multicomponent Assembly to Achieve Charge Separation and Transport for Energy Conversion

Daniel L. DuBois, Jun Liu, Xiadong Zhang

◆ The objective of this research is to construct organized multiscale materials containing arrays of nanorods, nanotubes, or nanochannels that allow for efficient electron and proton transfer over nanometer dimensions and to couple these nanoarrays with macroscopic objects, such as electrodes to molecular sites that can perform catalytic reactions. This capability will ultimately be required for efficient conversion of renewable energy sources (solar, wind) and fuels (hydrogen, methanol). ◆

Biological systems such as hydrogenase enzymes and photosynthesis integrate multiple components (such as catalytic sites, proton and electron transport channels, and light-harvesting centers) into functional assemblies. From a materials perspective, the question is, "Can we use our knowledge of the synthesis of new materials to achieve the properties that will be required to construct highly efficient devices for converting between electricity and fuels?" To achieve this goal, we have undertaken studies in two areas: proton transport in titanium oxide nanotubes and the attachment of molecular catalysts containing proton relays to metal oxide surfaces. The use of crystalline titanium oxide (TiO_2) nanorods and nanotubes may ultimately provide platforms for light-harvesting and proton and electron transport over distances of miro- to centimeters, and molecular catalysts can perform the same function as enzymes. The objectives of this project are to achieve the integration of the potential functional properties of TiO_2 by studying how proton and electron transport occurs in TiO_2 nanorods and nanotubes and attempting to attach molecular electrocatalysts to TiO_2 and other electrode surfaces.

Proton Characteristics and Transport Properties in Titanium Oxide Nanotubes. TiO_2 exists in the three ubiquitous phases (rutile, anatase, and brookite) and possesses an intrinsic wide-band gap (E_g ~3.0 eV for rutile and 3.2 eV for anatase), due to which both rutile and anatase adsorb ultraviolet light (typically ~5% of the spectral output of sunlight, while 45% is visible light). Narrowing TiO_2 band gap (red shift) appears as a straightforward approach to increase the spectral absorption of TiO_2 into the visible or even infrared region through chemically doping either Ti or O ions with other elements and/or tailoring TiO_2 morphology and size. In this research, TiO_2 nanotubes were synthesized by a single-step reaction between commercial P25 powders and NaOH in a hydrothermal reactor. The chemical formula of the acid-treated TiO_2 nanotubes was proposed to be layered $H_2Ti_nO_{2n+1}$ titanates. For $H_2Ti_3O_7$, the band gap was found to be ~3.3 eV; however, the oxygen nonstoichiometry was observed to vary in nanotubes depending on the synthesis and post-treatment conditions. As a result, the oxygen nonstoichiometry acts as dopant and changes the band gap, which in turn impacts electrical conductivity.

We recently employed solid-state ^1H MAS NMR to characterize proton concentration and dynamics in ZnO nanorods. Similarly, solid-state ^1H MAS NMR measurements of $TiO_{2-\delta}$ nanotubes were carried out. We were able to obtain high-resolution ^1H NMR spectra for $TiO_{2-\delta}$ using solid-state MAS-only NMR techniques. The observed sharp ^1H NMR resonances can be attributed to the hydrogen species in $TiO_{2-\delta}$ nanotubes. A significant reduction in spectral line width for the resonance peak at 6.9 ppm was observed when the temperature was increased from 25 to 250°C. The relatively high chemical shift (6.9 ppm) indicates acidity of protons in nanotubes. In this temperature regime, the peak sharpness is accompanied by an increased intensity. At 250°C, the resonance peak at 6.9 ppm is very narrow. The NMR line-width decreased as temperature increased, while the concentration of the 6.9 ppm peak stayed relatively constant over the temperature range. The significant line width narrowing observed for this peak may be the consequence of acid molecular motion hopping and resident proton site uniformity within the $TiO_{2-\delta}$ nanotubes. The dynamic measurements provide evidence for mobile proton species. Future research in this area will emphasize electrical conductivity measurements with possible blocking electrodes such as Nafion to separate electronic and proton ion conductivity.

Attachment of Molecular Catalysts Containing Proton Relays to Metal Oxide Surfaces. Several avenues for modifying metal oxide and carbon surfaces with molecular electrocatalysts for H_2 production were investigated. These catalysts all contain proton relays to facilitate the movement of protons from solution (or $TiO_{2-\delta}$) nanotubes to the active metal site of the catalyst. Four different approaches to surface modification were investigated: 1) simple adsorption, 2) the use of thin layers of ionic liquids containing the catalyst, 3) the use of ion exchange membranes such as Nafion for incorporating the catalyst cation, and 4) covalent attachment. For Methods 1, 3, and 4, immobilization on the electrode surface resulted in loss of ability of the molecular catalysts to undergo electron transfer reactions. This has been attributed to the restricted motion of the catalysts using these approaches. However, using thin layers of ionic liquids that resulted in redox active molecular catalysts and catalytic activity using modified electrodes for H_2 production was demonstrated.

Nano- and Micro-Engineered Solid Adsorbent for Rapid CO_2 Capture and Regeneration

Wei Liu, David L. King, Jun Liu, Bradley R. Johnson

◆ Success of this project will lead to CO_2 capture technologies with a 70% potential cost reduction to the conventional amine-scrubbing process for capture of CO_2 from combustion flue gases; representing a significant cost savings to U.S. industries if CO_2 capture and sequestration regulations are implemented. ◆

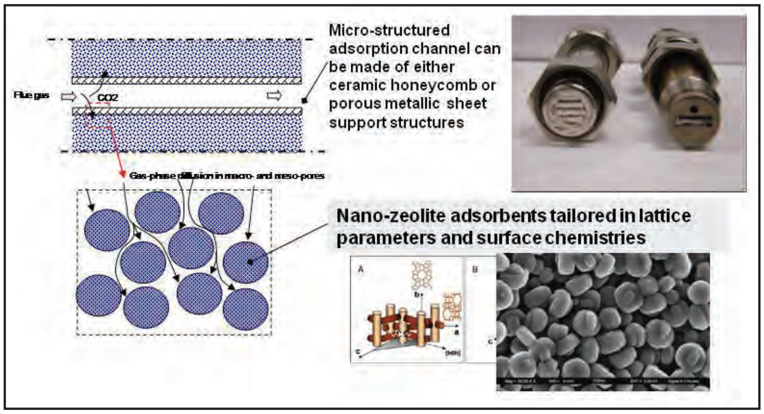
Various technical approaches to CO_2 capture have been reported in the literature, covering most separation technology areas including solvent absorption, solid adsorption, membrane, and distillation. Based on energy costs and process efficiency, adsorption is the most attractive for CO_2 capture from low-pressure, diluted flue gas streams, although certain technical liabilities must be overcome. Among all conventional and exotic adsorbent materials, zeolites have been selected due to an overall consideration of feasibility, innovation opportunity, durability, potential manufacturability, and ultimate costs.

This project focuses on adsorption technology for CO_2 capture from flue gas, which can provide immediate impact to existing CO_2 emission sources, such as power plants and refineries. Specifically, we are addressing critical problems associated with conventional adsorbents: slow adsorption and regeneration kinetics, lack of capacity and selectivity for a practical CO_2 gas mixture. The technical approaches we are using include: 1) developing cost-effective technologies for the synthesis of nano-sized zeolites that addresses one of key challenges in commercializing zeolite-based adsorbents by enhancing the intrinsic kinetics rate by two orders of magnitude, 2) innovation of specific frame-work or surface substitution of the zeolite lattice structure to reduce the heat of adsorption and increase the selectivity, and 3) developing micro-structured ceramic honeycomb adsorbent beds of advanced features, such as high adsorbent loading (>50 wt.%), low ΔP, and fast mass and heat transfer that are needed to achieve rapid adsorption/regeneration cycle and maintain long-term durability. Through development of novel nano-adsorbent materials and fundamental understanding of the necessary adsorption/desorption kinetics, this project will also lay the groundwork to development of new zeolite based pre-combustion CO_2 capture technologies (membrane, adsorption).

Project progress during FY 2008 included the following:

- A number of common zeolite materials were obtained and a few batch synthesis methods were evaluated to prepare the nano-sized Y, ZSM-5, and silicalite zeolite. Approximately 34 solid adsorbent samples were evaluated for CO_2 and H_2O sorption on a TGA apparatus.
- Nano-NaZSM-5 and silicalite prepared in this work show the highest CO_2 adsorption capacity and minimal H_2O sorption, while CO_2 adsorption on most commercial and literature adsorbents is severely inhibited due to moisture adsorption. Since water vapor is ubiquitously present in the CO_2 gas mixture, resistance of a solid adsorbent to moisture sorption is critical for a practically viable adsorption process.
- A flow adsorption/regeneration testing apparatus has been modified. Reversible, selective CO_2 adsorption of the present adsorbent was confirmed.
- Structured adsorption beds were prepared with two kinds of support structures: ceramic honeycomb and porous stainless steel sheet. 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.

FY 2009 research will focus on systematic understandings to correlation of nano-engineered adsorbent and micro-structured adsorption bed design parameters with adsorption/regeneration performances, particularly with simulated practical flue gas mixtures and under practical process conditions.



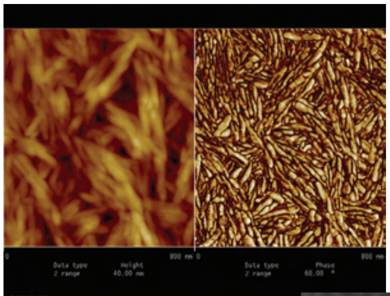
The adsorption working principles and key material innovations of the present technical approach are illustrated in the figure. As a CO_2-containing gas mixture stream such as power plant flue gas flows through straight channels at high linear velocity and minimal pressure drop, CO_2 diffuses across the macro-porous barrier layer into the nano-adsorbent packing zone and gets into contact with the nano-adsorbent particle that is fine-tuned in its surface chemistry and lattice parameters for selective adsorption of CO_2 over other molecules.

Nano-Crystalline Cellulose

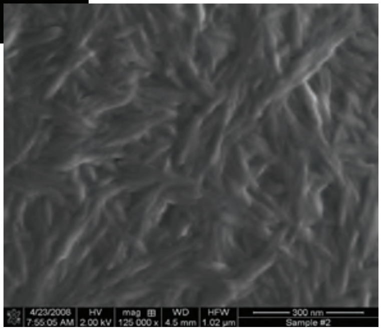
James D. Holbery, Cheng Huang, Dan Howe, K. Simmons

◆ Nanocrystalline cellulose synthesized from cellulose sources (wood fiber, bast fiber, leaf fiber, or cellulosic biomass crops [e.g., switchgrass]) offer an inexpensive reinforcement for applications such as polymer composites, a highly purified template for detection sensors, or a biobased coating reinforcement. In addition, nanocrystalline cellulose has the potential to be a value-added product from a future cellulosic biorefinery. Material projected to be waste from stock preparation and fermentation processes could potentially be converted to nanocrystalline cellulose and sold to chemical, health care, and materials supply industries. ◆

Cellulose is the most abundant renewable biopolymer on earth. It is a major structural polymer for plant cell walls and can be synthesized by some bacteria. Plant cell walls are composed of cellulose microfibrils aggregations embedded in hemicelluloses and lignin matrix. Using acid hydrolysis processes, the cellulose microfibrils can be disintegrated and separated into needle-like elementary crystallite, often termed cellulose nanowhiskers. The cellulose whiskers are ca 200 nm long and ~10 nm in diameter with characteristics that provide great reinforcing capacity. Nanocrystalline cellulose has a theoretical modulus estimated at 167.5 GPa measured at 143 GPa with a theoretical strength of 10 GPa. The technique to produce nanocrystalline cellulose is acid hydrolysis, upon which nanocrystalline cellulose becomes highly polar posing a challenge to disperse effectively without significant agglomeration during composite manufacture processes such as melt blending, extrusion, or film casting.



Topographic (left) and phase contrast (right) images of self-assembled liquid crystal textile structure of NCC nanowhiskers by tapping mode-atomic force microscopy.



Scanning electron microscope (FIB-SEM) image of thin film of NCC nanowhiskers.

PNNL began developing a capability in nanocrystalline cellulose in 2008. After conducting preliminary experiments, our results led to application specific development efforts that served as the basis for this project: to synthesize nanocrystalline cellulose from cellulose sources, reinforce urethane composites, and measure the mechanical properties. The outcome envisioned was to develop a laboratory capability in biocomposites.

This work proposes to use three switchgrass varieties and three bast fibers, including kenaf, hemp, and flax, as nanocrystalline cellulose feedstock sources. The motivation is to provide materials for a future cellolosic biorefinery by developing an inexpensive nanocrystalline cellulose fabrication process for biorefinery waste and secondary feedstock. Using switchgrass-derived nanocrystalline cellulose, our focus was to functionalize the pure surface of nanocrystalline cellulose to disperse the reinforcement within a polyurethane matrix, subsequently casting films from of the reinforced composite material. During the project, we accomplished the following:

- Established nanocrystalline cellulose processing capability, producing over 10 batches of nanocrystalline cellulose from softwood pulp explored using cellulose biofuel crops as a nanocrystalline cellulose source.
- Analyzed cellulose fibers and their constituents.
- Reinforced urethane polymer coatings with nanocrystalline cellulose and measured the mechanical properties of the films.
- Explored a new method to produce nanocrystalline cellulose using ultrasonic energy in place of acid hydrolysis.

We produced approximately 1 kg of nanocrystalline cellulose and analyzed material morphology, size distribution, and surface characteristics. Primary findings of the research include the following:

- Nanocrystalline cellulose acts as a reinforcement for urethane increases elongation at break from ~150-300% at similar stress levels. This is due to nanocrystalline cellulose arresting cracks that develop in urethane that if accurate could aid in other polymeric material performance.
- The hydrolysis technique used in this work produces repeatable crystals and can be scaled to industrial levels.

The production of nanocrystalline cellulose from switchgrass appears promising, though we believe further work is necessary to refine the bio-fiber processing.

Nanoporous Metal Phosphates as Alternative Cathode Materials for Batteries

Dawn M. Wellman, Vish V. Viswanathan, Daiwon Choi, Larry R. Pederson,
Shas V. Mattigod, Glen E. Fryxell

◆ Nanoporous metal phosphate materials offer a new class of compounds that are amorphous, corrosion resistant, and thermally stable. This research will develop novel nanoporous metal phosphates as alternative cathode materials for batteries to provide batteries with more energy-efficient capabilities compared to those based on crystalline technologies. ◆

The burgeoning global population continues to strain energy sources. Large-scale power outages throughout major metropolitan areas and increasing demands on foreign fuel sources have pushed energy research and technology development to the forefront within DOE to improve the efficiency, economy, and safety in energy generation, conversion, transmission, and use. Emerging technologies, such as the future grid will advance power reliability, and hybrid automobiles, will decrease U.S. dependency on foreign oil. However, to meet current energy demands, we continue to move toward dilute, sporadic power sources such as wind and solar energy. The primary obstacle hindering power sources such as these from alleviating current demands for power and widespread use of hybrid automobiles is more efficient energy conversion, storage, and use. The research proposed under this project is focused on developing nanoporous transition metal phosphates as alternative cathode materials for battery applications.

Recent investigations have indicated that an effective technology for enhancing battery performance is zero-strain materials, the lattice constant of which will not change during cycling. A side-by-side comparison of crystalline and nanoporous tin phosphate illustrated a greater initial discharge capacity, increased cycling, and a large capacity for the nanoporous material relative to the crystalline. The mesoporous structure alleviates the volume change during the alloying/dealloying process and appears to preclude the formation of lithium-tin alloys as observed in crystalline or glass materials. Additionally, nanoporous metal-phosphate materials exhibit enhanced corrosion resistance and the thermal stability that prevents over-charging.

Nanoporous metal phosphate materials offer a new class of compounds that are amorphous, corrosion resistant, and thermally stable. Our objective is to develop novel nanoporous metal phosphates as alternative cathode materials for batteries to provide more efficient energy conversion, storage, and utilization. Nanoporous transition metal phosphate materials are inherently more stable than crystalline materials, are not subject to phase separation, suppress dendrite formation, and allow more rapid lithium exchange.

In FY 2007, we developed a new tape casting procedure for battery cathode fabrication with nanoporous metal phosphate materials. Standard procedures were not amenable to the high surface area of nanoporous materials; as such, a significant number of iterations were performed, and necessary adjustments were made for the amount of binder and solvent added. Subsequently, electrode testing was conducted on lithium-iron phosphate nanoporous materials. Results indicated that approximately 60% of the theoretical capacity was attained, and the incorporation of carbon within the nanoporous structure allowed discharge at higher rates and increased the average discharge voltage.

In FY 2008, numerous nanoporous metal phosphate materials were synthesized and tested as battery cathode materials. Results of electrode performance tests indicated that iron and vanadium nanoporous phosphate materials provided poor capacity and displayed high self-discharging. Nanoporous vanadium phosphate exhibits structural stability issues under the harsh conditions encountered in electrode applications. Efforts to enhance the stability of vanadium phosphate by incorporating a small amount of tin increased the structural stability. Favorable electrode testing results indicated that the mixed tin-vanadium phosphate possessed a high capacity and stable cycle life.

During the course of this investigation, a number of nanoporous metal oxide materials were made in developing the synthetic procedure for nanoporous metal phosphates preparation with altered compositions and structures. Testing of these materials revealed that nanoporous vanadium oxide materials are highly promising cathodes that display high reversibility and rate capacity and are competitive with crystalline lithium cobalt oxide materials currently being used as cathodes. Continued pursuit of high-performance nanoporous vanadium oxides with various compositions (e.g., V_2O_5, V_2O_{13}) and structures is recommended. Additionally, nanoporous iron oxides displayed exceptional initial results as anode materials.

The results of this work have demonstrated that nanoporous metal phosphates and oxides maintain stable structures capable of undergoing repetitive cycling without crystallization or degradation during the intercalation and deintercalation of lithium. Moreover, the larger volume and porosity of nanoporous materials allow exchange of lithium at rates comparable to or exceeding that of crystalline "tunnel" structures in two directions.

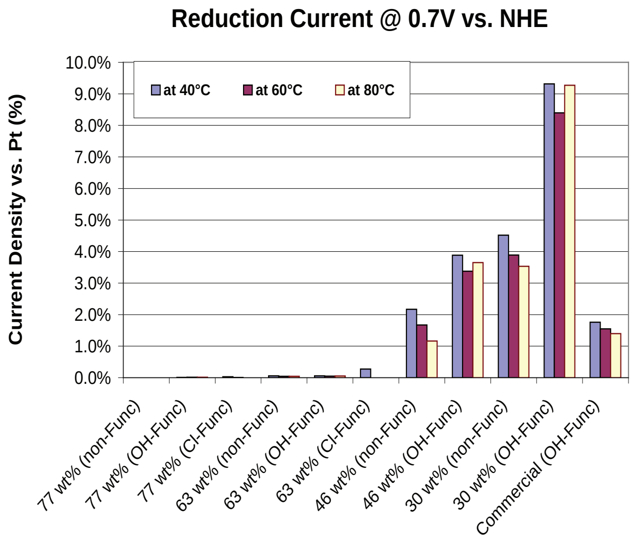
Nanoscale Tantalum Oxide Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells

Jin Yong Kim, Yongsoon Shin

◆ We intend to develop a method of synthesizing a heterogeneous nanoscale tantalum oxide electrocatalyst and are investigating the effects of microstructure and composition on its electrocatalytic properties, specifically with respect to the oxygen reduction reaction. Substantial interest can be generated with DOE in investigating the fundamental nature of these heterogeneous nanostructured materials in greater detail. ◆

Two key bottlenecks to the future success of polymer electrolyte membrane fuel cells (PEMFCs) are cost and developing an appropriate means of hydrogen storage. Recent economic studies indicate that PEMFC stack cost can be reduced dramatically by decreasing or eliminating the amount of platinum (Pt) required in the cell electrodes. While substantial progress has been made in understanding why Pt is such an effective catalyst for the oxygen reduction reaction, little success has been achieved in identifying promising alternative electrocatalysts. In FY 2008, we attempted to develop economical oxygen reduction catalysts for PEM fuel cells by replacing expensive Pt with tantalum oxide to enhance the catalytic performance of tantalum oxide by making nanoscale tantalum oxide/carbon composites that contain increased triple phase boundaries working as reaction sites for oxygen reduction.

Oxide anchoring involves the synthesis of nanoscale tantalum oxide and the formation of covalent bonding between oxide particles and a functionalized carbon support. Carbon black samples ~30 nm in size were treated with either nitric acid or thionyl chloride to form functional groups such as carboxylic groups on the carbon surface. Nanoscale tantalum oxide was synthesized using tantalum ethoxide and a surfactant to yield high-surface area powder mixed with functionalized carbon using a high-speed ball mill, revealing the formation of covalent bond between tantalum oxide and functionalized carbon confirmed by Fourier transform infrared spectrometry (FTIR). The shift of a peak related to carboxylic groups caused by the formation of covalent bonding was observed. Electrochemical analysis was conducted using a 3-electrode half-cell test setup with 0.1 N sulfuric acid as an electrolyte. The electrochemical performance of composite powders synthesized using the oxide anchoring method was not significantly different from a mixture of commercial tantalum oxide and carbon. Although the chemically synthesized tantalum oxide powder possesses high surface area, it forms the agglomerates of nanocrystalline tantalum oxide particles. Therefore, nanoscale oxide particles were not evenly dispersed on the carbon surface, resulting in limited triple-phase boundaries. Overall, mass specific reduction current measured at 0.7 V with respect to normal hydrogen electrode (NHE) is ~2% compared to Pt.



Mass specific current density of directly synthesized tantalum oxide/carbon composites measured at 0.7 V vs. NHE compared with Pt.

The second method we developed was direct synthesis, where functionalized carbon was dispersed in ethanol with tantalum ethoxide added. The functional groups on the carbon surface react with tantalum ethoxide, leading to condensation to form tantalum oxide *in situ*. The amount of tantalum oxide used was 30-77 wt%. X-ray diffraction and FTIR confirmed the evolution of a tantalum oxide phase and the formation of covalent bonding between the oxide and functionalized carbon. Since tantalum oxide is nucleated on the functionalized carbon surface, this method allows tantalum oxide particles to disperse evenly on the carbon surface. The electrochemical analysis conducted on composites synthesized by the direct synthetic technique shows an increase in catalytic performance with a decrease in tantalum ethoxide. When tantalum oxide increased, tantalum oxide appeared to cover the carbon surface so that the conduction of electrons through connected carbon particles is hindered. The maximum mass specific reduction current at 0.7 V vs. NHE was obtained from the composite containing the minimum amount of tantalum oxide (30 wt%). The mass specific reduction current of his sample was ~9% compared to Pt. For area specific reduction, this sample revealed up to 40% compared to Pt when five times of catalyst loading was used. Further study will optimize the electrochemical performance in terms of the amount of tantalum oxide.

Simultaneous Charge Transport in Laterally Confined One-Dimensional Systems

Xiao-Dong Zhou, Ed C. Thomsen

◆ In a conductor with reduced dimensionality, electron motion is free electron-like along the axis of one-dimensional systems 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, it becomes possible to discuss homogeneous transport properties in such reduced-dimensionality systems in the same context as homogenous transport in bulk systems. ◆

Homogeneous transport properties enable macroscopic phenomenological parameters such as mobility, conductivity, thermopower, and so on to be measured in appropriately designed experiments. Specifically, the density of states (n_{1D}) is inversely proportional to square root of energy (E) in a one-dimensional free electron gas, whereas in a three-dimensional system, n_{3D} is proportional to square root of E.

$$n_{1D}(E)=\frac{1}{\pi\hbar}2\sqrt{\frac{2m}{E}} \qquad \text{(1D system)} \qquad \text{(1a)}$$

$$n_{3D}(E)=\frac{m}{\pi^2\hbar^3}\sqrt{2mE} \qquad \text{(3D system)} \qquad \text{(1b)}$$

In a one-dimensional system, the density of states at the bottom of the band is much stronger than that in three-dimensional conductors; hence, it is possible to tailor electron transport property in one-dimensional conductors through control over material chemistry that impact the band structure and thus the density of states.

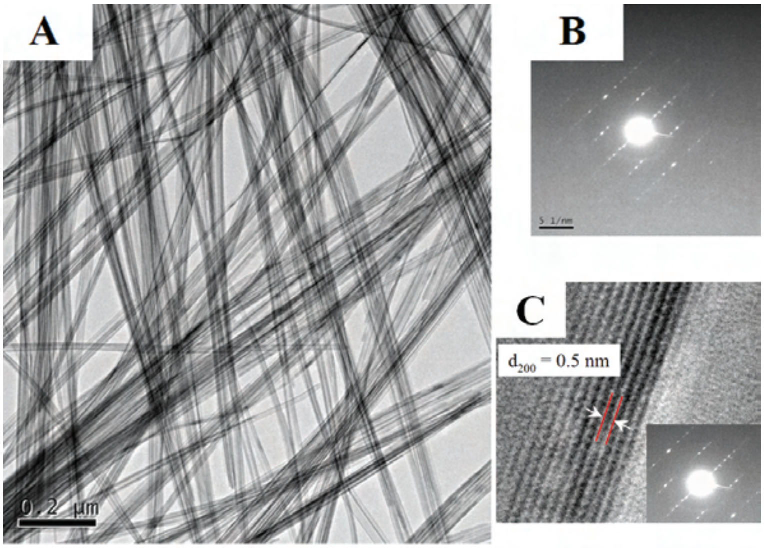
By contrast, ionic transport involving H^+, Li^+, O^{2-}, and F^- is quite different from electron conduction in low-dimensional systems with confined barriers. The difference arises because electrons move within sub-bands (Equation 1a) in nanostructured systems, whereas ionic transport often occurs via a hopping mechanism. Research on ionic transport in nanostructures has been controversial because of the complexities of mixed conduction and coupled intrinsic/ extrinsic doping effects. In an intrinsic system in which defects are formed through Schottky or Frenkel reactions, multi-layered thin BaF_2/CaF_2 films were created and observed with approximately 100 to 1000 times higher conductivity than in bulk specimens. However, in extrinsic systems in which majority defects are formed due to compensation of ionized extrinsic dopants, there exists a discrepancy of whether the ionic conductivity is enhanced or retarded. A recent systematic study showed that both *dc* and *ac* conductivity of YSZ can be enhanced significantly at a thickness of under 60 nm. There is no consensus regarding the transport of O^{2-} ions in nanoscale structures.

Although electron or ion transport alone in one-dimensional system is interesting, simultaneous electron and ion conduction (also called mixed conduction) is of more scientific interest, particularly within laterally confined systems on the nanometer scale. Equally important, mixed conductors are of considerable technological interest in a variety of energy conversion and storage arenas. Such materials entail a broader class of fundamental reactions that involve charge exchange and transfer between electrons and ions. Charge transport and associated reaction form a fundamental basis for energy interconversion of fuels (chemical), photons (solar), phonon (thermal), and electrons (electrical).

Results on ZnO. An exemplary mixed conducting system is ZnO, whose nanowires have been vigorous because of the feasibility of the fabrication of various morphologies and unique electrical/dielectric properties. Two fundamental unanswered questions center around the origin of n-type conduction and the characteristics of protons in ZnO nanowires. The n-type conduction has been attributed to intrinsic defects (such as Zn interstitials and/or O vacancies) or the presence of hydrogen. However, this issue remains controversial. With respect to the characteristics of protons in ZnO, we recently employed in situ nuclear magnetic resonance (NMR) to investigate proton dynamics in ZnO nanorods. Protons are clearly present in ZnO at ambient temperature; however, protons remain in ZnO at elevated temperatures (between 200-500°C) only in some highly aligned and uniform nanowires.

The transport dynamics of protons associated with defects in the lattice of ZnO nanorods can be determined from measurements of the temperature-dependent spin-lattice relaxation time T_1. Since we can differentiate the signals associated with these proton defect states from the weakly-bound surface hydroxyl groups, site-specific dynamic information can be obtained. Measured T_1 is displayed for the 4.8 ppm resonance as a function of temperature. The activation energy and correlation times are obtained by fitting the measured T_1 as a function of temperature using Equation 2. The nucleus of ^1H has a spin of ½; hence, it is reasonable to assume that the inter-proton dipole-dipole interactions dominate spin-lattice relaxation. T_1 can be expressed as:

$$\frac{1}{T_1}=C\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right),\ and\ \ \tau_c=\tau_0\exp\left(E_a/RT\right) \qquad (2)$$



A) TEM image of MnO_2 nanowires, B) selected area diffraction of MnO_2 wires, and C) lattice fringe image.

Here, τ_c is the mean correlation time for proton hopping, ω_0 is ^{1}H resonance frequency, and C is the dipole-dipole relaxation constant. From our measurements, we obtained $\tau_c = 2.2 \times 10^{-9}$(s) at 300 K and 2.1×10^{-10}(s) at 500 K. The activation energy is ~0.15 eV. The small activation energy and short correlation time indicate that those protons are mobile.

One of the common features that protons and lithium ions share is relatively low activation energy (E_a) for hopping. The E_a for proton hopping in ZnO nanorods was found to be ~0.15 eV from in situ NMR measurements, assuming that the inter-proton dipole-dipole interaction dominates spin-lattice relaxation. This activation energy (0.15 eV) is approximately one-third of that found in high-temperature proton conductors. The phenomenon of increasing proton mobility leads us to answering the research question of whether we can controllably design a one-dimensional system so that Li ion hopping is enhanced. This research question is of substantial importance in understanding ionic transport in confined oxides and advancing materials development for energy storage systems.

Results on Manganese Dioxide (MnO_2). The MnO_2 nanowires were synthesized by oxidation of manganese sulfate with ammonium persulfate in a hydrothermal reactor. The precipitates were then filtered and washed for further characterization. Electrical conductivity was measured in an alumina die with a pressure of 100 MPa via a two-probe dc technique. Magnetization was measured by PPMS. MnO_2 is known with different allotropic polymorphs denoted by α, β, γ, etc., which differ in the way of the distribution of Mn ions in the octahedral sites of oxygen framework. Both x-ray and electron diffraction indicated that the as-synthesized MnO_2 phase is α-MnO_2. The figure illustrates TEM images of as-synthesized MnO_2 nanowires, which have an average diameter of approximately 20 nm. Selected area diffraction, lattice fringe image, and dark field image showed that each MnO_2 wire was a single crystal.

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 stream of data 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 data sources be accessed to solve a particular problem, that more information be known about the history and derivation of the data, and that the data can be readily exchanged between various analysis programs that are often constructed as processing pipelines. The intention of this project is to define an architecture that uses semantic technologies and is 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.

In FY 2008, we developed and deployed the Describe Anything API (DAApi), our goal for which is to provide a powerful recording interface that supports automatic graph relationship management and is flexible enough to apply to a variety of execution models. The DAApi interface defines the core capabilities of the API, including basic storage. The WorkflowDAApi extension handles session management, and storage calls can be made for either one or a number of resource objects. Actual storage is delegated to alternative implementations of the ProvenanceProvider interface, the second component of the interface. We support both URIQA and JMS providers, with the latter offering asynchronous recording essential to high-throughput workflows. The third and optional part of the interface is ContentProvider, which enables capture of physical files to the content store or an archive.

To determine the completeness of our architecture, we investigated six use cases and documented compelling examples of benefits that provenance can provide for a diverse set of domains. These cases provided new functional provenance requirements that were contributed to the International Provenance and Annotation Workshop community.

Finally, to support provenance browsing, we surveyed existing work related to browsing Resource Description Framework (RDF) stores. From our analysis, we selected the product Longwell, which is web-based and provides alternative views such as faceted search, timelines, and graphs. While many tools exist, defining a graph view that is intuitive to arbitrary RDFs is an open research problem. With multiple existing and a framework for adding views, Longwell provides a promising RDF for developing custom views. To test Longwell's applicability to our work, we collaborated with nuclear magnetic resonance experimentalists, harvesting metadata on over 15,000 experiments and simulations and augmenting Longwell to support editing and linking of experiment and computation. Our conclusion is that while Longwell is promising, its performance is not adequate for use with such large data sets, and custom development will be required to provide views that make sense to particular users. Thus, future tool development must emphasize both view development and scalability.

Our focus on provenance is key unifying mechanism to describe, annotate, and track relationships between data and to search for data in disparate data sources while retaining autonomy between sources. Semantic technologies and standards such as RDF will be applied from the ground up to create a basis for semantic queries and reasoning. Experience and software from previous work on SAM will be incorporated into architecture but with an emphasis on high performance to meet the needs of MeDICi.

This effort is highly complementary to other LDRD efforts in that the provenance component will be directly applicable to workflow execution with provenance capture. The data virtualization architecture will be developed generically so that it can easily be applied to other scientific domains such as global climate change, groundwater modeling, computational chemistry, homeland security, geoinformatics, and engineering applications.

Our goal in FY 2009 will be to extend the provenance server to support extensible graph queries and to bundle the DAApi, browser, and provenance storage engine as an off-the-shelf capability for provenance capture, storage, and searching.

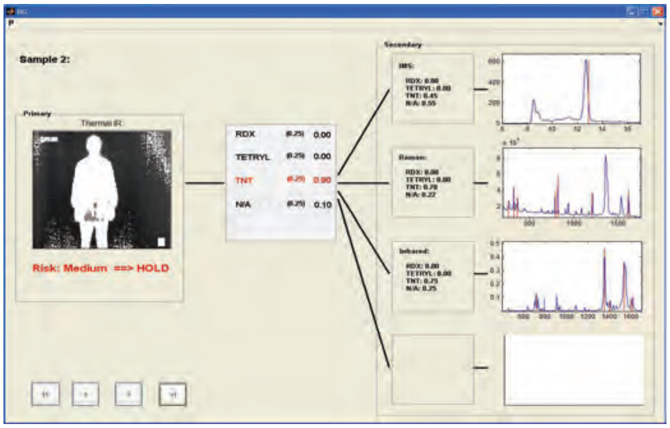
A Statistical Framework for Integrated Explosives Detection

Kristin H. Jarman, Nathaniel Beagley

◆ 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 being developed for preconcentration and standoff and trace level explosives detection. Developed to work alone or in combination with other sensors, these technologies work to 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 two-stage (primary and secondary) explosives detection. This framework will be able to propagate uncertainty through a multi-sensor detection system and perform Bayesian integrated explosives detection. A prototype for this framework will be developed and tested on data from publicly and privately available sources.

An initial explosives detection framework was developed and demonstrated on a limited dataset. A *Bayes network* forms the framework basis that models the propagation of uncertainties from primary through secondary screening, incorporates dependencies between different sensors, and allows threat probabilities to be passed between the two screening stages. From this model, the traditional *junction tree engine* algorithm is used to take sensor measurement data and propagate through the network to provide likelihood scores associated with different threats as well as benign materials. These scores are used to determine the presence or absence of an explosive.



Sample 2:

Primary

Thermal IR

Risk: Medium ==> HOLD

RDX (0.25) 0.00
TETRYL (0.25) 0.00
TNT (0.25) 0.90
N/A (0.25) 0.10

Secondary

IMS:
RDX: 0.00
TETRYL: 0.00
TNT: 0.45
N/A: 0.55

Raman:
RDX: 0.00
TETRYL: 0.00
TNT: 0.78
N/A: 0.22

Infrared:
RDX: 0.00
TETRYL: 0.00
TNT: 0.75
N/A: 0.25

Matlab prototype framework for two-stage explosives detection. Primary screening consists of thermal IR imaging, and secondary of ion mobility, Raman, and IR spectroscopies. In primary, thermal IR imaging show anomalous materials on the subject, recommending a hold. In secondary, the three different spectroscopic measurements are compared with signatures of explosives of interest. All individual measurements are integrated using a Bayesian network, resulting in a high likelihood score for TNT.

In FY 2008, the focus was on two-stage detection with primary and secondary screening. In the primary stage, individuals, cargo, or other items are passed through rapid, stand-off explosives detection methodologies. Items or individuals with anomalous or suspicious measurements are flagged for secondary screening, where those flagged items or individuals are subject to additional detection methodologies designed to look for more specific threats with the highest possible sensitivity and specificity. An example of such a screening process includes an airport security check where all passengers and their carry-on luggage are subject to initial stand-off threat detection using metal detectors (passengers) and x-rays (luggage). Passengers with unusual or suspect readings are passed to secondary inspection, which consists of additional passenger search, bag search, and possibly explosives detection using commercial ion mobility spectral detectors.

The two-stage explosives detection framework was developed in prototype development software (Matlab). It was demonstrated using data available from other projects in the initiative, including thermal infrared imaging data and ion mobility, infrared, and Raman spectras. Demonstration of the framework was made using data for three explosives: RDX, TNT, and tetryl. In FY 2009, this framework will be extended to a variety of different operational scenarios. In addition, a performance and sensitivity study will be conducted using a combination of simulated and real data to demonstrate the benefits of this approach over traditional data analysis methodologies.

This project directly addresses the need for sensor integration and decision-making algorithms in the area of explosives detection. It applies PNNL's expertise in sensor decision analytics to PNNL's strong capabilities in highly selective materials and advanced instrumentation. The work will greatly expand on a sensor integration scheme developed at PNNL for microbial forensics by generalizing the methods into a framework that can be used to evaluate a variety of different sensor configurations and tailoring the scheme to problems unique in trace and stand-off explosives detection. The successful development of this framework will accompany and strengthen other projects under this initiative and will help position PNNL as a leader in integrated explosives detection systems.

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 or complete description and retrieval of information, thereby enabling scientists and analysts to manage information more efficiently. The benefits of this research are demonstrated in the context of anomaly detection in computer networks and object identification and property correlation in satellite geophysical data. ◆

In recent years, advances in hardware technology have facilitated the ability to collect massive amount of data continuously. This has led to a number of computational challenges: 1) algorithms are only allowed one pass over the data streams, 2) algorithms must cope with the temporal evolution of streams and can no longer hold all the 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 is required.

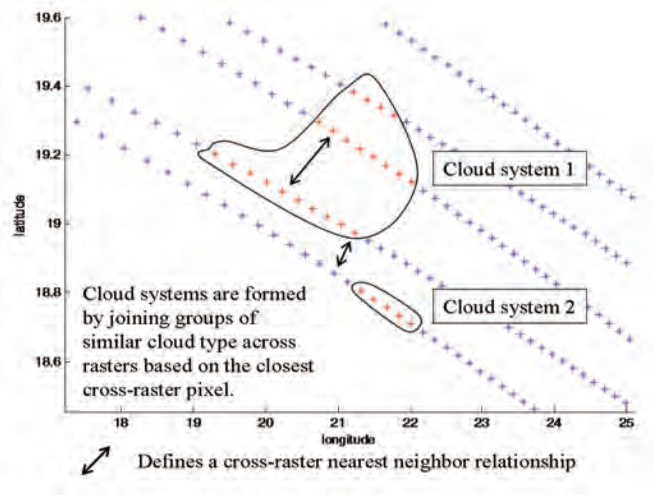
Attempts at organizing and comparing fusing techniques for streaming data have been made only very recently. These efforts highlight the need for a framework within which rational fusion strategies for streaming data can be developed. The objectives of this project were to develop foundations of such a framework and to 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 to measure statistical relationships between object properties.

We developed a comprehensive, five-level taxonomy (classification) that characterizes not only the inputs and outputs of a fusion system but also the relevant fusion processes and algorithms. This taxonomy forms the backbone of the 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. By making it adaptive and robust, we improved its detection rate of true anomalies as shown in early benchmark testing. Moreover, the confidence level or degree of anomaly measurement was calculated to provide a quantitative assessment of the uncertainty associated with the anomaly detection. We also 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 the evaluation of 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. This fusion detection work is the object of a patent application, has been published in a peer-reviewed publication, and has been presented at two conferences.

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, which 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 developed in the first year of this project, the satellite fusion work falls under symmetric feature fusion. First, we are identifying objects (e.g., clouds and cloud layers) and matching objects between data sets; next, we will be merging the measured features of those objects to perform statistical analysis.



Example of cloud system identification from individual points.

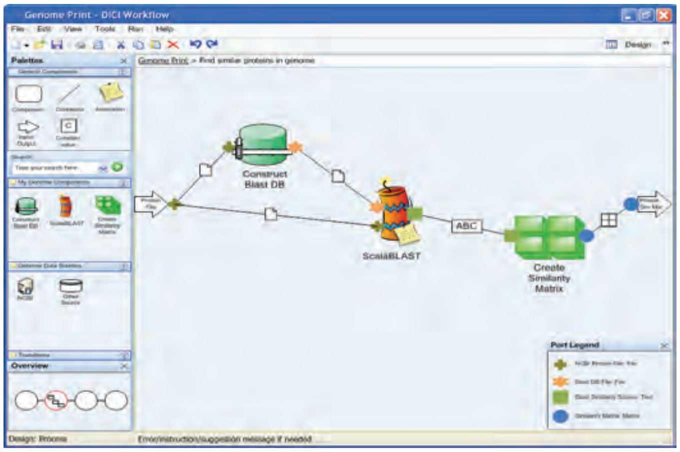
Adaptive Workflow in Data Intensive Elements

Alan R. Chappell, Ian Gorton

◆ This project produces a workflow design and management capability that will enable researchers and analysts to exploit massive data sets and specialized compute facilities. This workflow system supports the 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 and 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 inundates current computation and communication infrastructures. Knowledge extraction, access, and storage of massive data require a change in how we analyze the data 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 has been used as a mechanism for enabling more flexible composition of these components. While the definition of workflow differs, it can be generally defined as the order and restrictions in which steps in a process are performed. Beyond descriptions, workflow management systems support the automatic execution of a described workflow. By supporting the use of workflow in data-intensive environments, researchers, analysts, and decision-makers may be able to make more effective use of massive data sets, high-performance and special-purpose computing facilities, and collaborative inputs from other complex systems.



A screen from the visual design for the workflow system interface showing user interaction to create computational pipelines.

In FY 2007, we focused on system requirements and technology assessment, selection, and prototyping. Existing workflow technologies and systems were found to be inadequate to handle data-intensive environments and to be used by non-specialists. To address these deficiencies, we chose an approach that involved the use of an open standard Business Process Execution Language (BPEL) 2.0 supporting workflow management technologies for component orchestration in conjunction with the MeDICi Integration Framework to provide the underlying computational architecture. A prototype implementation of this system demonstrated that the design exploited the strengths of both technologies and enabled a flexible and powerful computational environment.

Based on this foundation, work in FY 2008 focused primarily on the design and development approaches for user interface and interaction systems. One of the primary goals for this research is to develop a system that supports the involvement of non-specialists in the creation of workflows. Our experience with BPEL editors reinforced that all classes of potential users found the editors to be cumbersome and overly complex. To develop a more generally usable system, we employed a user-centered design process of the workflow interface. In a series of design sessions, users completed a series of exercises during which they discussed their need for workflow systems, illustrated concepts of how such systems might look, and provided feedback on designs that merged ideas from across sessions and domains. Based upon interactions, we created a series of visual designs that map proposed interactions in the use of the workflow system from creating, running, debugging, and reviewing previous runs.

The workflow system under development is complex. Traditional approaches to creating such a system would be expensive and produce a large code base that would be difficult to evolve. The model-driven architecture (MDA) approach is beginning to address these issues through the systematic use of information models and mappings to create robust and maintainable interactive systems automatically. Using emerging MDA environments and tools, an initial implementation of the workflow interface based on the design enables a user to work with visual artifacts at a familiar level of detail to draw a computation pipeline. Using MDA capabilities, the system automatically updates a workflow model based on this interaction. When ready, the system transforms this model into a BPEL workflow model that can be deployed to a BPEL execution engine. Future work will expand MDA boundaries to the capabilities of this interface and system to incorporate a larger set of the capabilities from the interface design, including adaptive computation. This work was reported in one book chapter, one refereed conference paper, 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 is 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 drive U.S. competitiveness. ◆

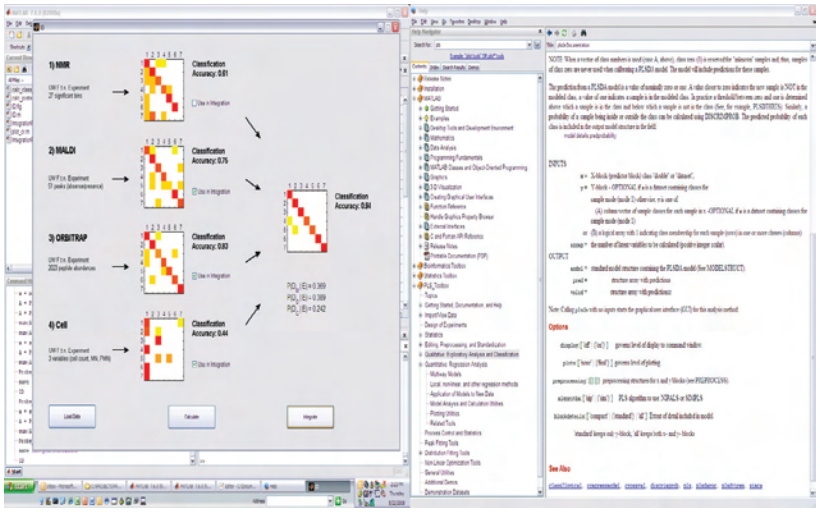
With the end goal of inferring system level biological activity, data integration is one of the challenges of modern biology. Though biology is often a data-rich discipline, integration can fall short because of complex data types that lack one-to-one mappings (e.g., proteins to genes). Specifically, 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 peaks on a spectrum. Integrating data from multiple technologies into an interpretable form to identify either a diagnostic pattern or the underlying biological response requires developing and using powerful statistical approaches to manage 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 are developing a Bayesian statistics framework, a powerful property of the ability to introduce prior knowledge into the model. However, this is challenging because all experimental data must be represented as probability models. Building the framework requires four core technical developments: 1) an interface for access to disparate data sources, 2) probability mappings of the data to perform Bayesian integration, 3) diagnostic models of exposure or response, and 4) derivation of biological models for biomarker discovery. 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. Additionally, we developed a visualization for communicating results to scientists performing the experiments.

Rapid Response to Biological Agents. In this experiment, mice were exposed to one of three organisms: *Francisella tularensis* ssp. *novidica*, an avirulent mutant of *F. n.*, and *Pseudomonas aeruginosa*. The mice were evaluated using four approaches at 4- and 24-hour periods to determine if exposure markers were present at a pre-symptomatic state: 1) proteomics by high resolution mass spectrometry, 2) proteomics via matrix assisted laser desorption ionization, 3) metabolomics via nuclear magnetic resonance, and 4) cell count data traditionally collected in most immunology laboratories. We demonstrated that the integrative approach could improve the classification accuracy of the mice into exposure groups to 89% over 83% for any single high-throughput proteomic and metabolomic dataset. Adding cell count data improves the classification accuracy further to 94% despite the data having poor discriminating power individually as seen in the figure.

Ecosystem Change in Response to Perturbation. In this experiment, a periphyton community as exposed to U at four doses (unamended, 10 μg/L, 100 μg/L, and 500 μg/L) over the course of five days. Following collection of the periphyton, the biomass was extracted and sent for phospholipid fatty acid and mass spectrometry-based proteomic analysis. Probability models were derived for each technique, resulting in classification accuracies of 80% and 87%, respectively, for each method. The integration of these two datasets improved the overall classification accuracy to 96%.

In FY 2009, we plan to develop an iterative algorithm to identify key signatures from each dataset that improve overall classification. Such a model will identify a subset of potential biomarkers as the most fruitful candidates for continued analysis. In addition, we will use both data at a global scale, as well as these candidate markers for biological modeling in the demonstration problem spaces.



Visual integration for Bayesian evaluation allows the user to evaluate multiple probability models in both an independent and integrated manner.

Characterization Model for Defense Adaptability

Chad O. Hughes, Bryan H. McMillan, Steven J. Ouderkirk, Harlan P. Foote, Randy L. Bosetti, Branden M. Rolston

◆ This research aims to develop algorithms and methods to develop a computer network model that can be used to make judgments as to the normality of the system. ◆

Current approaches to detecting novel (or zero day) attacks on digital enterprises often depend on traditional anomaly detection, protocol deviations, or a combination of the two. Anomaly-detection approaches typically begin by characterizing the normal behavior of users through the processes they run within a specific environment. This characterization is compared with observed behaviors to identify any that deviate from the norm. Behavior in this context usually means observations of network traffic generated by human interaction with applications or monitoring of host-based activity generated by such human interactions. A parallel technique is used for characterizing activity not so directly drawn from human interaction, such as a host's operating system or other automated processes.

While such approaches have been reasonably effective in the past, they are known to be subject to training-based attacks. Opponents are able to escape detection if they can skew the characterization of "normal" behavior to incorporate elements of their intended misuse; observations of their behavior would then fit within the normal profile. It is potentially feasible to achieve this skew effect without internal access, in far less time and with far less access and knowledge of defenses by leveraging very large scale attack systems (such as botnets). Because the usefulness of anomaly detection is expected to deteriorate if novel attacks are to be anticipated in time to intervene, it will be necessary to use a method that does not depend upon behavior characterization that can be skewed from the outside.

This research examines a new approach to predicting novel attacks through the identification, observation, and characterization of the underlying network entities and rather than focusing on observations of the surface behavior of those who use a network. These network entities should be less subject to the skew effect, since they are based on the identification of the network actors supporting the infrastructure regardless of how it is used. Network entities will be identified by observing the actual integrated working of a target digital information infrastructure and inductively classified. The scope is to explore a new approach of measuring and classifying network traffic to determine how much of the originating environment can be reconstructed using only the structure observable in raw network traffic. It will do this by building classification frameworks for both first order (identifying entities on a network by activities they perform) and second order (identifying the goals, intent, and social relationships of those entities) behaviors. This will enable technology advancements in areas like cyber deception, anomaly detection, and cyber exercises.

The result of this research was to break the current practice of identifying important issues with a network and making decisions reactively. The characterization model for defense adaptability takes the inverse of this approach. First, observations are the primary driver, and entities are identified as sets of correlated actions observed within context. Classification frameworks are employed to discover both the first and second order behaviors. Finally, emergent qualities are binned and used to form value judgments to impact dynamic security enforcement.

In FY 2008, we obtained and investigated 2.5 terabytes of an operational network. During the investigation, we used spectral analysis to transform and explore the dataset. We were able to identify promising features deductive with only information in the headers of flow data. We have also used a self organizing map approach to explore inductively the second order behavior of the entities or actors within the dataset. The current method is to analyze network traffic in an attempt to identify and react to anomalies. By definition, this is typically done using expert opinion without a concrete understanding of ground truth. Using a spectrum, two groups can be formed: those who can make intelligent guesses and those who have the authority to make decisions. Communication through the spectrum, however, may cause loss of credibility. The current process attempts to deal with the emergent qualities of the network based on value judgments and the possible impact due to implicit policy. From there, static classification frameworks based on individual protocols and activities in theoretical use are employed. Lastly, policy driven controls are modified during an observation phase.

The primary input to the process is Pcap data and SiLK tools (header characterization is our initial approach). Eventually, deep packet and session characterization will follow. The characteristics are fed to several mathematical transforms to identify data clusters that will be analyzed to categorize their significance to the original flows extracted from Pcap. The elements deemed significant are then used to create a model. We then use a simulator to create an environment representative of the network in question. Sensors placed in the simulator collect the new traffic, which is analyzed and compared with the original data to validate the model. Work remaining involves writing a paper for publication that will describe the mathematical approach by which we will extract second-order structures (clusters) from computer network traffic flows and measure their validity (covariance).

Complex Adaptive Agent Resilient Cores

Devin E. Smith

◆ Complex adaptive systems will be required to protect systems against a complex adaptive adversary. These systems must possess a high level of trust at their core with respect to adhering faithfully to an internal model designed by authorized developers to protect against unauthorized modification, co-option by an adversary, or inadvertent goal reorientation due to unanticipated circumstances. The objective of this research is to identify and examine resilient models from nature to supply core building blocks required by future implementations of defensive systems that must operate in hostile environments. Without these resilient cores, unpredictable non-linear responses may result, causing mission failure. ◆

Current protection models approximate the dynamic environment in which they are expected to operate and are either brittle with respect to small variations in parameter values (an over-defined situation) or do not respond appropriately to large variations in parameter values (under defined). A complex adaptive adversary may force an oscillation between these two extremes, causing a system failure without foreknowledge of the algorithm in use. Resilient cores should not be violated in either of these situations. Ideally, these resilient cores will employ features such as protection of the internal model, neighboring sensors recognizing that a change has occurred in the internal model within the system, and changes in the collective behavior should be observable (if not measurable).

As a starting point for exploring how these features could be used within a cyber context, work done at the University of Washington was consulted in the modeling and simulation of the metabolic pathway (Segment Polarity Network [SPN]) of the fruit fly (*Drosophila melanogaster*) using ordinary differential equations demonstrating the appropriate features. High interest was generated because there was robust emergence of patterns during the fly's developmental stages while the environment changed in dynamic ways. This was the starting point for exploring how these features could be used within a cyber context.

Project accomplishments during FY 2007 included the identification of the SPN as a solid starting point for the development of generalized dynamical networks (resilient cores) for use within the I4 initiative. One area identified for possible use was support of artificial homeostasis. In addition, a limitation of the SPN was the required richness of observables and number of interacting nodes. The correspondence to processes within Microsoft Windows, for example, was difficult establish. Two paths were identified: apply the problem to a more complex setting or engineer a reduced model that operated in a simplified parameter space.

FY 2008 achievements include examining the SPN model in detail. The SPN appears as the third stage of fruit fly cell development and the first involving multiple cells. The SPN pattern establishes orientation (polarity) and boundaries (segments) for multi-cellular features developed later. The boundaries are two cells wide, marking the end of one segment and the start of the next. The boundaries survive cell division and return to a narrow two-cell pattern.

The SPN model accepts a wide variety of parameters while still demonstrating a segment polarity pattern. Generation of random values for the approximately 50 parameters in the SPN yields a surprisingly high fraction of stable SPNs. Further examination of the model shows a set of three primary interacting feedback loops. Initial conditions were observed to be significant and required realistic values to induce stable SPN formation. The feedback pattern included positive feedback, a feature not typically associated with biological models. The three primary feedback patterns are positive feedback from initial cell conditions only, positive feedback requiring initial cell conditions and transport from a neighbor cell, and the absence of sufficient initial conditions with negative feedback to dampen any potential change.

A reduced SPN model was developed and explored that focused on the three primary feedback patterns. When starting with the three primary feedback patterns, initial concentrations determine whether a cell will activate as a boundary cell. It is a model that once configured denies all changes. If an SPN model was watching communication ports, those not active (between SPN boundary cells) would not be allowed to switch to be active regardless of precursors such as data arriving at input or output buffers. An SPN system requires restarting with new initial conditions to allow new behavior.

The SPN model demonstrated adaptive behavior on cell division. Active feedback patterns in the doubled boundary cells were shutdown by lack of supporting feedback and communication with neighbors. If an artificial event happened to turn "on" a normally "off" port, the lack of supporting feedback of the surround ports would damp and eventually deactivate the port. The SPN model can act as a homeostatis mechanism, but its primary feedback pattern is positive rather than negative. A system reset is required to allow change. The observed SPN robustness is due more to a small number of dominating parameters pairs than by inherent flexibility or adaptability. As such, the SPN model is not rich or complex enough to develop further as part of a complex adaptive system.

Computational Biology and Bioinformatics Tools for Understanding the Role of Membrane Proteins in Diurnal and Circadian Processes of Prokaryotes

Christopher S. Oehmen, Jason E. McDermott, Lee Ann McCue, Bobbie-Jo M. Webb-Robertson, Ronald C. Taylor

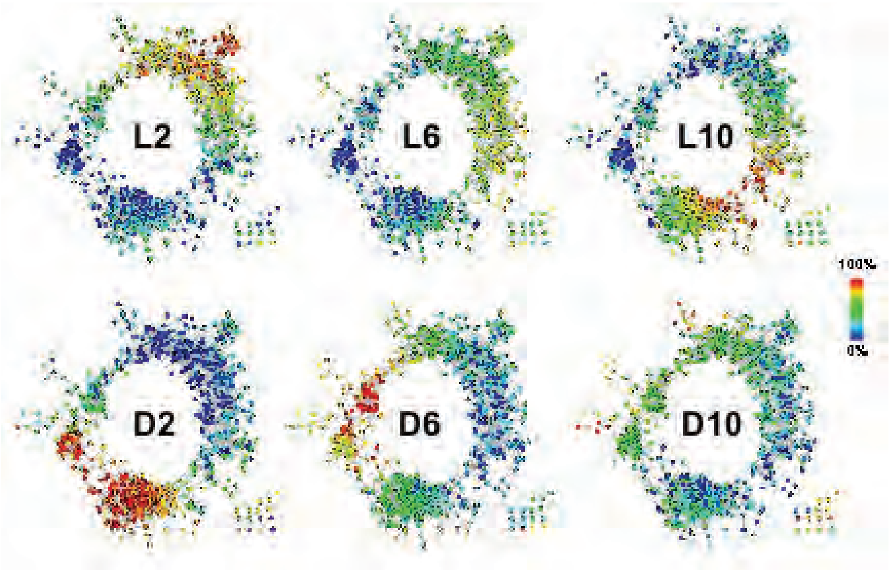
◆ Identifying and developing renewable energy sources relies in part on the ability to identify mechanisms for processing carbon in the environment. This project is an approach to understanding carbon handling at the level of molecular interactions and membrane systems of single-cell organisms, which have shown great potential as agents for carbon sequestration. ◆

Cyanobacteria represent a large fraction of the total biological mass on earth, so they are potentially a powerful target for renewable energy production and environmental cleanup. The genome of *Cyanothece*, a cyanobacteria that synthesizes energy using two separate and incompatible mechanisms of nitrogen fixation in dark and photosynthesis in light, has been sequenced only recently, as part of this study. Other cyanobacteria perform this feat by compartmentalizing the different processes in different specialized cells. But *Cyanothece* separates nitrogen fixation and photosynthesis temporally in each cell, having to switch its molecular machinery twice daily to accommodate this separation. Often, it is the presence or absence of light that in part triggers changes in an organism. In this case, *Cyanothece* evidence points to time-dependent processes in which the cell switches based on its internal mechanisms as if anticipating rather than reacting to the light/dark cycle. This process is rooted in the genetics of *Cyanothece* because switching between nitrogen fixation and photosynthesis (and vice-versa) requires extensive remodeling of the cell's molecular machinery. It would seem that this is a great effort to expend on cellular reorganization, yet *Cyanothece* is a highly efficient organism.

In FY 2008, we focused on applying analysis methods developed in prior years to: 1) *Cyanothece* time course proteomics data, and 2) data from cell division studies. We pursued two independent lines of analysis for the time course proteomics data. In one approach, advanced statistical models were developed to account for a variety of bias sources including instrument drift. The result was that a collection of cycling proteins were identified, a key step in confirming that the protein content does in fact follow the previously identified cycling pattern for genes in *Cyanothece*. Finding these cycling proteins leads us to understand which functions or processes are turned off and on during the normal daily cycle of *Cyanothece*.

The second approach was to use relevance networks similar to how they were previously applied to transcriptomics data to orient the proteomics results for many of the proteins found with respect to the daily cycle. In this approach, individual cycling proteins are not identified, but the cyclic relationship between the whole protein complement can be visualized as a closed loop. Layering functional information onto this representation illustrates where in the cycle each function is active.

For our second analysis area, cell division was postulated to have a strong dependence on the diurnal cycle. This hypothesis was confirmed experimentally in a series of studies in other companion LDRD projects. Physiological, chemical, and proteomic data were collected from these experiments. The computational aspects of studying cell division include identifying genes and proteins (and ultimately pathways and processes) that are turned "on" in anticipation of cell division. Statistical and analytical techniques used in the diurnal cycling aspects of the study were used to confirm that a large class of proteins expected to participate in cell division were in fact most prominent just before cell division. Expected research would focus on understanding the molecular events which differentiate cells that divide from those that do not.



Genes of Cyanothece naturally fall into a wreath configuration using Pearson correlation and imposing a threshold of 0.925. Genes are colored by their expression at the indicated time point (L=light, D=dark, number=hours between 0 and 11). The wreath analysis accurately maintains the temporal arrangement of the data and provides a high-level temporal overview of global expression levels.

Computational Capabilities for Storage, Management, and Utilization of Large Data Volumes

Keqi Tang, Erin M. Baker, Nathaniel Beagley, Bill Danielson III, Anoop M. Mayampurath, Richard D. Smith

◆ The next generation proteomics measurement instrument platform (LC/ESI/IMS/TOF MS) is capable of generating data at extremely high speed (~100 Mbytes/s) due to its unique high throughput sample analysis capability. The focus of this project is to develop and implement new computational capabilities for effective managing of the massive volumes of proteomics data from the new instrument. ◆

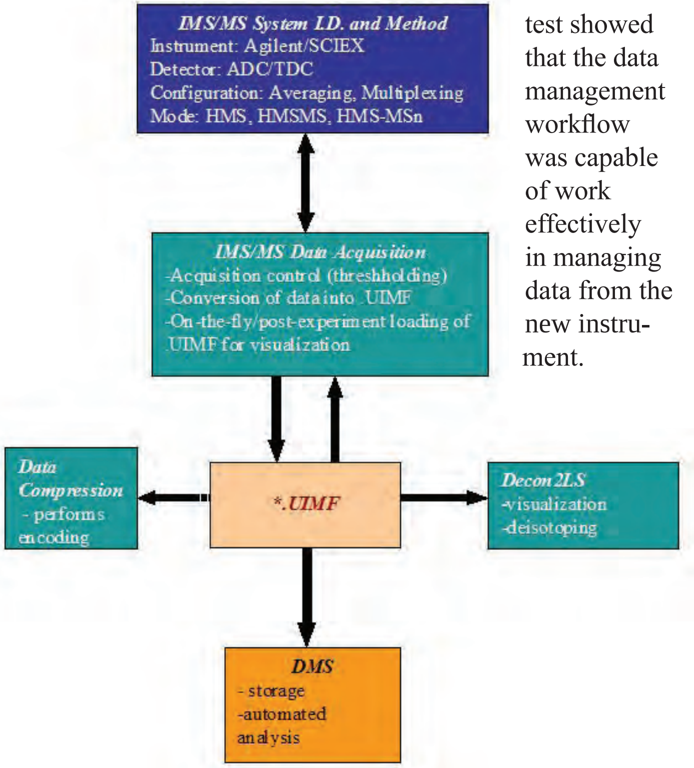
This project focuses on developing new computational capabilities for real-time data processing and display. The new software tools are developed to handle effectively the extremely high data generation rate by the next generation proteomics measurement platform. The developed data handling capability also includes efficient data compression, storage, and management necessary for subsequent data analysis.

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 condensed-phase (liquid or solid) separation and high performance mass spectrometry (MS) can achieve very high resolving power (peak capacity >500 for single-stage separation methods and ~3000 for multi-dimension separation methods). The major limitation of these technologies is their low sample throughput, mainly due to the low speed of separation in the condensed phase.

To improve the proteomics measurement throughput, PNNL and other research institutes developed the new instrumentation that combined ion mobility spectrometry (IMS), a gas phase ion separation technology with MS. Using PNNL's patented ion funnel and multiplexed IMS technologies, the sensitivity of the IMS/MS instrument was improved significantly. The key feature of IMS is the extremely fast speed of analyses: an IMS separation typically takes less than 0.1 s, much faster than LC separations (minutes to hours). Combined with MS, IMS/MS can offer a comparable separation power as LC/MS with a 10- to 100-fold increase in throughput. The major challenge is to handle the massive volume of data from the instrument effectively. For example, a single LC/ESI/IMS/TOF MS analysis may have 1000-10,000 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, which is impossible to use the current methodology for data management.

Under this project, high performance data management capabilities for the new proteomics measurement platform have been developed and tested for initial proteomic applications. The new software tools for efficient data compression and storage will be fully integrated in FY 2009 with the current computational architecture to handle effectively the high data generation rate (~100 Mbytes/s) by the new instrument platform.

During FY 2008, the data management project was focused on developing new software tools needed to support the data volumes generated from the IMS/MS system and to move and access this information in an efficient way. Specifically, the development of the effective data management software tools started from the instrument data acquisition process. Signal thresholding was applied during the IMS/MS data acquisition to reduce the data transfer rate. The data file was converted on the fly to a unified data format (.UIMF) for efficient post-acquisition data visualization. The raw data files acquired from the IMS/MS instrument were further compressed to retain only the essential information sufficient for subsequent informatics analysis before they were stored in the data management system. As shown in the figure, the initial test showed that the data management workflow was capable of work effectively in managing data from the new instrument.



New high throughput proteomic measurement platform (LC/ESI/IMS/MS) data management workflow.

Correlation Layers for Information Query and Exploration (CLIQUE)

William A. Pike, Shawn J. Bohn, Wendy E. Cowley, Joe Bruce

◆ Across domains, the need to analyze high-volume streaming data visually is central to creating human understanding of patterns and trends in that data. The Correlation Layers for Information Query and Exploration (CLIQUE) project is developing analysis techniques that can help detect features embedded in these streaming data sets, such as anomalies in computer network traffic. ◆

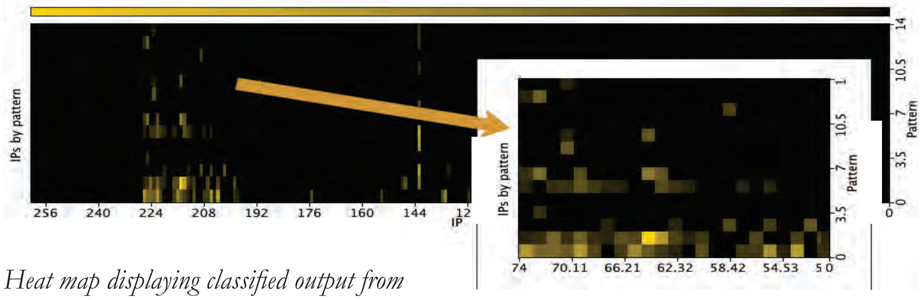
The objective of the CLIQUE project is to develop new visual analysis methods that help humans discover and detect potentially malicious events in vast amounts of streaming data. The project will develop a set of software components that implement new algorithms for pattern discovery and new visual metaphors 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-based use general heuristics and statistical variances to identify patterns of interest. In practice, however, neither method alone is sufficient.

Recognizing that a gap exists between signature- and anomaly-based approaches, we are implementing a set of machine-learning algorithms for use in either a supervised or unsupervised mode. Rather than producing visual displays that depict all of the raw data, we use a multi-level classification approach to reduce and condense data visualized to an amount more suited to human interaction. The goal is to classify the data into patterns that represent categories of behavior inherent in computer network data. These patterns are further classified based on temporal sequence to create higher-level abstractions of network activity. Coupled with a visual front end, this multi-level classification approach 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.

To develop a multi-level classifier, our approach applies unsupervised classification to aggregate network flow records into natural behavioral groups and then uses 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. A decision-tree classifier in this toolkit produced categorizations accurate to 97% based on a sample of test data with known outcomes but it is unable to model discrete variables with large numbers of categories, making it unsuitable for our data.

Using heat maps, we show how low-level transactions are grouped into higher-level behaviors and yet higher-level patterns. 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 multi-level classification. As heat maps are typically static, we are developing a dynamic heat map display capability that will allow analysts to track the high-level behavioral patterns in streaming data.

As part of our FY 2008 work, we 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. In FY 2009, we will implement a functional prototype for an analytic environment that helps users understand the traffic patterns in streaming data. The analytic environment will be composed of multiple coordinated displays that provide insight into the dynamic nature of streaming data. We will modify the current heat map visualization to allow it to evolve over time as patterns in the incoming data change. In addition, we will build another visualization that supports the depiction of behavioral trends. We will introduce a dynamic space filling curve to maximize the visual space over the analyzed time span. This display will give the user the ability to analyze a much greater quantity of data within a constrained space, thereby resulting in new visualizations that can scale to the increasing volumes of data characteristic of computer security problems.



Heat map displaying classified output from 23 million network flow records showing Internet protocol address (x-axis) versus behaviors identified via CLIQUE classification (y-axis). Cell saturation indicates frequency of observation for a given behavior. The heat map allows identification of actors engaged in a particular behavior as well as those behaviors that tend to co-occur.

Data Intensive Machine Learning for Real-Time Decision Analysis

Bobbie-Jo M. Webb-Robertson, Christopher S. Oehmen

◆ This research supports DOE's mission to build and operate major forefront scientific user facilities. Improved learning classification methods on data-intensive applications that can be deployed in real-time will enable advanced warning systems to protect the nation's critical infrastructure, including energy, cyber networks and development of computational models of protein function relevant to energy production and bioremediation. ◆

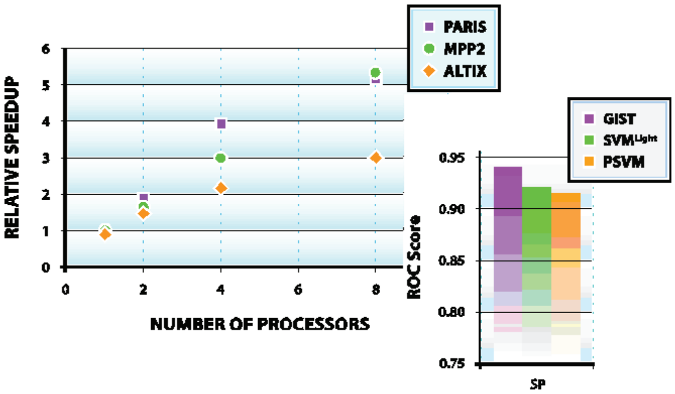
Making rapid and accurate decisions is a key capability required for applications as diverse as radiation portal monitoring and biological hazard detection. In both cases, it is necessary to classify events as "requiring attention" or "normal" so that the proper response can be taken. This classification is often performed using rule-based decisions. Machine learning is an attractive alternative to rule-based methods because it uses statistical learning techniques that make it possible to separate the computational complexity of analyzing enormous heterogeneous datasets from the act of decision making. Support vector machines (support vector machines) have been shown to be robust and accurate machine-learning classifiers compared with other learning algorithms such as neural networks. The improved performance is the result of using the kernel method to transform the original data into high-dimensional and optimization in this new space.

There are many freely available support vector machines codes with implementations of varying granularity in the core optimization task, the performance of which is related to four key elements: 1) the size and dimension of the data set on which they are operating, 2) the granularity of their core support vector machines optimization implementation, 3) the kernel transformation applied to the data, and 4) the underlying hardware on which the implementation is running. To assess the performance of different support vector machines implementations, several freely available codes representing the spectrum of optimization granularity were built on a variety of hardware: two Linux clusters and a shared memory machine. Binary classifiers were trained on datasets of varying size containing anywhere from a few hundred to over 50,000 vectors. Methods performance was measured in terms of wall-clock time for training, statistical quality of the resulting classifier, hardware performance (memory footprint, memory bandwidth, floating point unit usage, I/O bandwidth, and instruction stalls), robustness, and portability.

Support vector machine training involves finding hyperplanes that approximately bind the data classes, maximizing the distance between these planes and identifying vectors that lie near the hyperplanes, which can be accomplished mathematically in a variety of ways. We evaluated the three most common serial implementations that solve this problem (GIST, LIBsupport vector machines, and support vector machines^{Light}), as well as a recently introduced parallel version, Psupport vector machines. For each of these methods, we evaluated a spectrum of training datasets from small (2.4 MB) to large (26,925 MB) on a variety of computer architectures, including a small 10-processor Linux cluster, a large 1960-processor supercomputer Linux cluster, and a large shared memory Altix machine.

Overall, we discovered a trade-off between accuracy and speed. The figure shows the relative speed-up of each of the platforms using the parallel implementation of support vector machines for up to 8 processors on the small cluster (PARIS), large cluster (MPP2), and large shared memory machine (ALTIX) on a relatively large dataset (2753 MB). It scales relatively well; however, as the inset shows, it does not perform as well as the other algorithms in terms of the area under a Receiver Operating Characteristic (ROC) curve, which gives an overall measure of accuracy of the classifier (an ROC score of one would be a perfect classifier). LIBsupport vector machines reported class membership alone (not raw scores), so the area under the ROC curve could not be calculated for LIBsupport vector machines. GIST was consistently the best classifier by this metric regardless of dataset. Support vector machines^{Light} and Psupport vector machines had nearly equal ROC scores for each classifier. As the datasets grew, the support vector machines^{Light} and Psupport vector machines derived classifiers performed more similar to those trained using GIST.

This research resulted in five referred journal publications, two referred conference publications, a special session at a high-profile bioinformatics conference, and a book chapter on recent progress in machine learning.



Relative speedup of training on the SP dataset (2753 MB) using Psupport vector machines on multiple processors and overall accuracy compared to serial implementations.

Data Network and Policy Modeling: A Methodology for Modeling and Application of Network Policy

Craig A. Goranson

◆ This project will help practitioners generate network security policies that couple their high-level intentions to enforcement mechanisms selected from a database of best practices. The intent is to enable agile network security policy maintenance in today's dynamic environment. ◆

Existing network policy implementations require the practitioner to write and enforce policy via a variety of languages tailored to each tool and separate from overall organization intentions. We propose a policy framework model that will unify separate network security policies under a single language that links high-level intent to low-level enforcement. We will predefine best practices for enforcement of various intentions to allow users to express their desires without being concerned about the technical details of enforcement. The objective of the framework model is to make policy easy to maintain, responsive to changing business demands, and flexible to the diverse computing environments found in today's business networks.

We began with a statistically-defined network model and used information from network sensors to infer the sensed network security state. As expressed in the intent codified in policy, we compared the sensed state to the desired state. If the sensed state violates any policy intentions, we select mitigations and enforcements from a list of potential actions associated with each policy intention. We chose mitigations that have minimal cost and impact on the fulfillment of other policy intentions.

In FY 2007, we examined the role of policy in network security and surveyed how current best practices succeed or fail in dynamic environments. We derived a framework model that reasserts the importance of policy intent and uses dynamic assessment to validate policy compliance. We also defined a method to quantify risk, need, and intent across diverse networks and equipment. Finally, we engaged domain experts to create best-practice mitigation rule sets for policy enforcement and developed a prototype policy framework model implementation called the Entity-Policy-Enforcement Engine (EPEE). The result of this work was a strong understanding of network security policy best practices and the gaps in current policy management methodologies. The most important lesson was that the business intent underlying most security policy often becomes separated from the true business need by policy implementation. Our policy framework model allowed us to specify policy intentions and link them to best practice mitigations. Economic drivers such as market activity, acquisitions, and business model variations cause changes in business needs. In turn, business needs drive the high-level intentions used to derive policy. We define network security policy as a formal specification of business intentions expressed in terms of cost (risk, need, and value) and mapped to mitigation methods (equivalent enforcement means). We implemented a rudimentary policy expression language and a prototype monitoring enforcement engine.

The research conducted as part of the project for FY 2008 focused on the derivation of dynamic states through the mapping of dependencies and the effect on risk throughout a policy model. When moving past a static to a realistic network model, we addressed the significant potential for direct and indirect dependencies to effect aggregate risk. These dependencies had to be quantified to allow modeling of potential policy costs and impacts across a given environment as either a single policy or network architecture change could have a positive or negative cascading effect. The research identified several key concepts of a network policy model that attempts to assess dependencies relationships. Indirect dependency relationships were found to be convenient for summarizing relationships but were not easily used to equate risk and value cascades. Direct relationships could be assessed though the attribution of risk and value from dependent components to their dependency root. This methodology established that aggregate risk flows in the direction from dependency toward the dependent system, while component value flows in the opposite direction.

The advancement of methodology by identification of dependencies and dynamic assessment of aggregate risk provides a framework by which a changing network environment can be modeled. These dependencies and relationships can be either learned through network monitoring or formalized change control procedures inside the network environment.

The differences between perceived operation of networks and their physical reality can be significant and pose serious problems if not sufficiently addressed. The goal of this research was to provide a quantitative model to provide near real-time awareness of network environments, systems values, and security practices across the network. The methodology from this research and the EPEE engine have shown that it is possible to model risk and value in highly complex and dynamic environments and can be manageable and maintainable.

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

Z. Fred Zhang, Lirong Zhong, Mark D. White, Y. Fang

◆ This project will develop an aqueous-gas multi-component operational mode of the STOMP simulator to reproduce multi-component gas transport and the chemical reactions between gas components and contaminants. The developed code can be used to simulate the in situ gaseous reduction (ISGR) 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. ◆

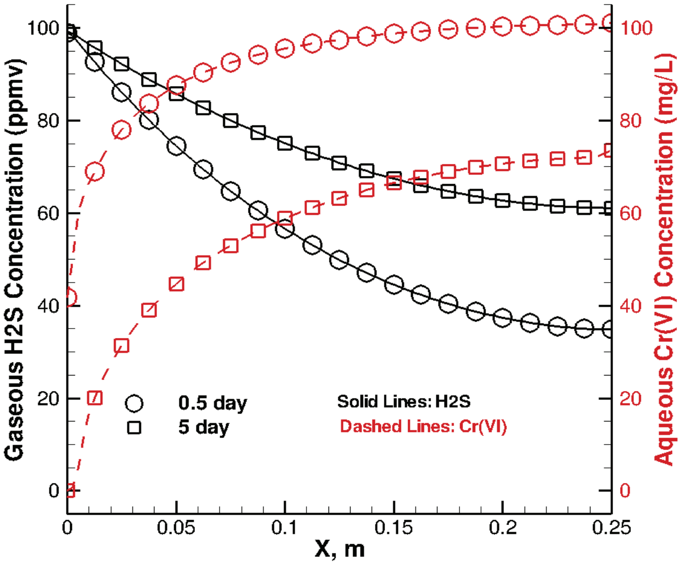
A large amount of radioactive contaminants resides in the vadose zone of Hanford and other sites around the country. PNNL has developed the in situ gaseous reduction remediation technology to immobilize redox-sensitive contaminants in the deep vadose zone using a diluted hydrogen sulfide (H_2S) gas mixture with nitrogen (N_2). However, this technology has not been used due to DOE's concern about the safety of toxic H_2S during the remediation process.

The current version of STOMP can simulate the movement of only one gas component. A module to simulate chemical reactions, ECHE-Chem, has been created. This project will develop an aqueous-gas multi-component operational mode of STOMP that allows the user to specify gas components and allows for those components to react. The outcome of this project will be a new simulation capability added to the STOMP simulator. The new code can be used for the optimal design of the ISGR remediation network and the safe implementation of remediation.

During FY 2008, we developed an aqueous-gas multi-component operational mode of the STOMP simulator as STOMP-WNE (Water-N-components-gas-Energy) to simulate the transport of gas with one or more components in the vadose zone and coupled the newly developed STOMP-WNE with the reactive transport module ECKEChem as STOMP-WNE-R to simulate chemical reactions during the gas transport process. In addition, we used the developed code to simulate the transport of the mixture of oxygen (O_2), N_2, and H_2S, a displacement process of nitrogen by methane (CH_4), and the reduction of chromium-VI [Cr(VI)] by 100 ppm_v H_2S in N_2. We found that the developed code can correctly simulate the transport of multiple-component gas and the reactions between gas and aqueous components.

To apply the developed code for any practical use (e.g., to guide an ISGR remediation design and implementation), further work needs be completed. Specifically, we need to continue the development of a numerical simulator, and test and debug for all the newly developed input options (e.g., boundary conditions, source terms, initial conditions related to gas components, and reaction species). We also need to verify STOMP-WNE and STOMP-WNE-R with laboratory experiments, and apply the code to simulate existing experiments. A few laboratory experiments of Cr(VI) reduction by H_2S with the sediments from Hanford or elsewhere have been conducted. The developed STOMP-WNE-R will be used simulate these experiments in FY 2009.

The expected outcomes include a fully tested and verified software STOMP-WNE and STOMP-WNE-R packages, comprehensive experimental data, and a draft manuscript for a peer-review scientific journal. The code is expected to be usable for field ISGR applications. Additionally, the code can be used to simulate multiple-component gas transport in a landfill, nuclear repository, or CO_2 sequestration site.



Simulated H_2S and Cr(VI) concentrations at two different times when Cr(VI) was reduced with 100 ppm_v H_2S.

Developing a Knowledge-Centric "Simulation Backplane" for Multi-Physics Simulation with Nuclear Energy Applications

Robert S. Butner, Patrick R. Paulson, Tara D. Gibson

◆ This project enables collaboration within multidisciplinary teams involved in technical modeling and simulations, such as those involved in climate studies and the design of power generation facilities. Through a framework for formal descriptions of model parameters, the project enables the development of a common vocabulary that reduces engineering design delays by improving the usefulness and accessibility of engineering models. ◆

Many research problems entail solutions that span a wide array of disciplines as well as a range of physical phenomena and scales. Harnessing computer simulation and modeling on such problems presents unique challenges, including model integration at different scales and domains. Facilitating information flow between domains, disciplines, and scales may pose an even larger problem both scientifically and institutionally compared with many challenges faced in focused domains. Integration of models focused on atomic-level phenomena with mesoscale of the overall fuel rod system poses similar scaling challenges along spatial dimensions and must be linked across disciplinary boundaries.

This research demonstrates a new approach to modeling and simulation development that helps address the challenges of integrating models and simulations across problem domains. The project provides a framework that exposes the semantics of scientific and engineering simulations via a simulation backplane that allows engineering and scientific models to be queryable with respect to the physical meaning (semantics) of model parameters, input data, outputs, and underlying assumptions.

We developed a software architecture for an enterprise-level framework capable of linking ontologically-based knowledge stores with conventional data sources (simulation tools and artifacts such as input and output files as well as configuration data; relational databases; semi-structured data sources; and unstructured data such as web documents). This framework facilitates semantic linkage and interoperability between such data sources and knowledge stored using explicit semantic constructs in the Web Ontology Language (OWL). The framework supports the model description made available as web services in a service-oriented architecture. It provides access to the models through existing semantic web APIs and a wiki-based user interface that can be used to import external ontologies and semantically annotate web services.

The project team extended semantic media wiki to allow editing domain ontologies (formal vocabularies) for annotating web services. These extensions include the ability to include the import of external formal ontologies for the description of models and the ability to extend and annotate ontologies dynamically from within the Wiki environment. We also created software to automate the conversion of Web Services Description Language documents to OWL, enabling documentation of a web service within the semantic wiki, which provides an environment for formally documenting model semantics and input and output parameters.

The following outcomes can be expected from the proposed work:

- Development of a white paper identifying key modeling and simulation challenges posed by fuel performance modeling that will provide a brief discussion of past efforts on fuel performance code development and identify simulation needs at a domain level as well as an effective use of models in an engineering environment.
- Development of an enterprise-level architecture for managing research and development endeavors knowledge. This framework will facilitate semantic linkage and interoperability between such data sources and knowledge stored using explicit semantic constructs such as ontologies and semantic graphs.
- Implementation of a prototype semantic introspection API to link simulations that will support basic functionality range, including representation and persistence of high-level knowledge constructs such as goals, assumptions, and hypotheses; a reasoning engine; facilities for semantically enabled resource discovery; and resource publication/event notification.
- Development of nuclear fuel performance models using the simulation backplane API to foster a small number of new simulations that address a specific aspect of fuel performance.
- Extension of the Backplane concept to address simulation interoperability.

Future efforts will to be to explore the more fundamental computer science issues posed by the goal of automated or semi-automated integration of simulations across widely differing scales, solution techniques, and physical domains. Such challenges go beyond the needs addressed by current efforts and require advances in applied mathematics and computer science.

Development of Core Informatics Analysis Tools for Confident Protein Identification and Quantitation

Gordon A. Anderson, Joshua N. Adkins, Brian H. Clowers, Navdeep Jaitly, Brian L. Lamarche, Anoop M. Mayampurath, Richard D. Smith

◆ Proteomics is the study of the protein complement of an organism. Unlike the genome, an organism's proteome is a highly dynamic system that contains information on its condition, including indicators of stress. To uncover this rich information from biological samples, it takes high-performance instrumentation and perhaps demands high-performance software tools. This research will result in the next generation analytical tools to enable discovery of proteomics profiles. ◆

The identification of peptides and proteins in biological samples requires high performance and high-throughput instrumentation. Mass spectrometry (MS) is a technique used in many laboratories, including PNNL. New developments in gas phase separation (ion mobility) coupled with the liquid chromatography (LC) time-of-flight mass spectrometer have the ability to analyze more samples than lower performance systems in a given period and generate significant volumes of data. This new capability cannot be fully exploited without new analysis tools to extract the features from the raw data and to identify these features using information from biological databases.

Research performed on this project is aimed at developing new and advanced feature-detection algorithms to characterize the important information present in the raw data. Additional developments will allow these features to be identified using a database of information. For example, a database of peptides and its characteristics can be used to identify a feature found in raw data. To enable this capability, software tools are both being developed and existing tools embellished. This research will develop the advanced analysis pipeline that will extract the important information from the raw data and enable the biological discovery helping DOE to address critical issues such as bioenergy and carbon management.

To enable the required data analysis capability, novel analysis tools and new algorithms are needed. Accomplishments are focused in a number of critical areas:

Feature Detection. Algorithms were developed and demonstrated to analyze multidimensional datasets, as well as detect and characterize all features present in multi-gigabyte data files. These algorithms define the key parameters necessary to assign these features later to a peptide. The features are often low in signal intensity and require processing technique to enable detection.

The key step in feature detection is de-isotoping, the process of detecting peptide signature in the MS data and characterizing these features for later alignment and identification. PNNL has developed Decon2ls to perform this de-isotoping process for FTICR data. Decon2ls is the main component used in IMS-MS feature detection with the addition of new capability in an AIMS application to measure and characterize the feature's drift time.

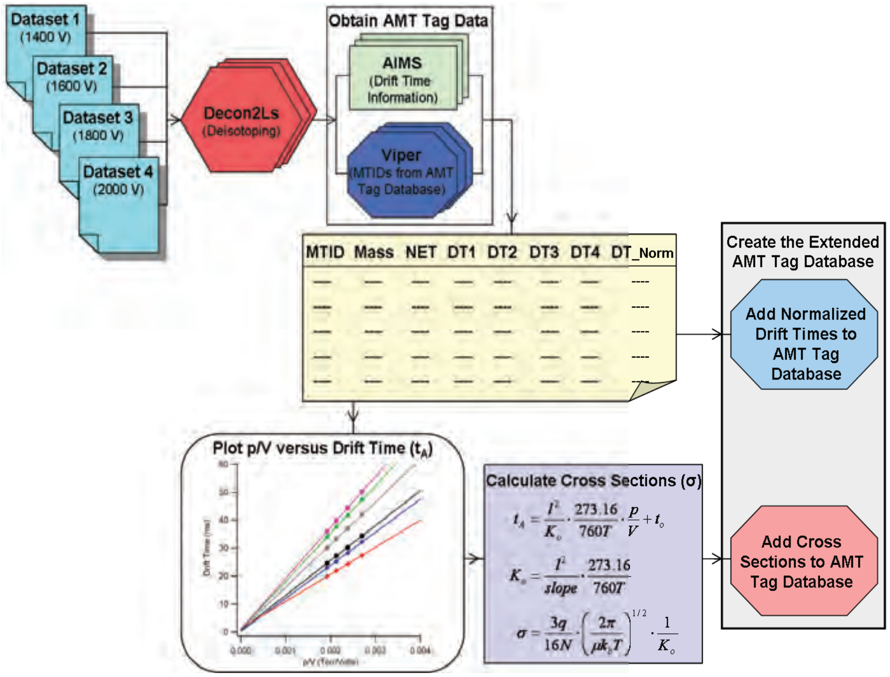
An additional capability is necessary for the analysis of MS/MS data: the ability to correlate the parent peptide mass and its fragments. This step is necessary to generate a parent and fragment mass list for use in peptide identification algorithms such as SEQUEST, X!Tandem, or InSpect, to name a few. We have started initial evaluation of these tools, and further evaluation and development in this area is planned for FY 2009. Currently, the best performance has been achieved using capabilities present in ICR-2LS, which was developed at PNNL. Features are grouped into sets of individual features representing an individual peptide or other chemical species. These assemblies are referred to as Unique Mass Classes, clustering that was expanded in our VIPER software to support the additional dimension of drift time.

Feature Alignment. Identification and comparison of multiple datasets require the alignment of the features present to each other in these multidimensional datasets. A technique was researched, developed, and demonstrated that performs alignment on the liquid chromatographic axis using our LCMSwarp algorithm and adding a linear regression to perform alignment on the ion mobility drift time axis. This results in a fast, robust alignment technique. This two-step process has been demonstrated on experimental data, where instrument parameters we varied to create miss alignment deliberately, thus allowing characterization of the two-dimensional alignment.

Prediction. In order to use an existing database of peptide identifications, it is necessary to predict the gas phase drift times. This is a complex problem, and two approaches were researched: the use of machine learning algorithms and the calculation of cross-section (and thus drift time) using high-performance computing capability and computational science algorithms. Both the machine-learning approach and the calculation of the cross-sections technique are promising and show positive initial results. Each method provides its own challenges, and further research is necessary to determine the optimal approach. The machine-learning approach

Identification and Training Data. To use the AMT tag approach in conjunction with IMS, the drift time information from IMS must be added into the AMT tag database. This drift time determination for each peptide can be performed either by measuring the drift times experimentally (and thus building a database with the measured drift times) or predicting the drift times using peptide sequence data as well as other peptide physical characteristics. For existing AMT databases, the ability to predict drift time would allow high throughput quantitative measurements to be performed without the need to generate new AMT databases. For future AMT database generation, the IMS-MS capability will allow drift time measurement using the MS/MS analysis pipeline.

In order to develop a predictive capability and validate performance, a large set of training data is necessary to support the development of all informatics efforts. This training dataset was developed using tryptic digests of *Shewanella oneidensis*, depleted mouse and human plasma samples analyzed with LC-IMS-MS using a 10-hour LC gradient. All three samples were collected at four different IMS drift cell electric field strengths, and a new software program was developed to extract the median drift times and calculate the peptide cross-sections so that the process could be automated. The software program calculated the cross-sections by plotting the peptides' extracted drift times (t_A) at each electric field voltage as a function of pressure over electric field (p/V). t_A versus p/V plots are always linear, with correlation values of at least 0.9999 and slopes that match the ion's cross-section.



The process for adding IMS drift time information in the AMT tag database. First, datasets from the four electric field voltages were deisotoped. The deisotoped features' monoisotopic mass and NET were then matched to the existing AMT tag database so that each mass tag identification (MTID) could be aligned with its four plotted drift times. After certain filtering criteria, cross-sections were calculated for each MTID, and normalized drift times at 1.8 kV were added to the AMT tag database.

The benefits afforded by adding the IMS dimension to the AMT tag database were examined by assembling the IMS information for the tryptic digest of *Shewanella oneidensis* into a mock database with 2049 mass tags. An experimental dataset for *Shewanella oneidensis* separate from the ones used to construct the database was matched to the mock database with two different filtering criteria. First, filters were placed on mass and NET (9 ppm and 0.01) but not drift time and second, filters were placed on all three criteria (drift time tolerance of 0.46 ms). In the case with no drift time filter, the false positives were found to be 7.12%, while if filtering was performed on all three dimensions, the false positives dropped to 3.19%. The observed 50% drop in the FDR is encouraging for future data analysis with the extended AMT tag approach.

Further information about each peptide was also found by analyzing the cross-sections. A linear relationship was observed between drift time and m/z for each specific peptide charge state, and little or no overlap occurred between charge states. The slope, intercept, and deviation of each charge state line was compared with the three samples. In all cases, almost identical line parameters for specific charge states were observed (e.g., the +2 peptide charge state line for *Shewanella oneidensis* had a slope, intercept, and deviation, similar to the +2 peptide charge state line for depleted mouse plasma), indicating that each peptide charge state behaves similarly no matter what sample they are from. These results were promising for formulating drift time prediction capabilities for peptides in multiple datasets as long as the m/z and charge state are known. Current work is being done to generate and characterize a peptide drift time prediction algorithm. If the prediction is successful, it would be used as an additional filter to remove false positives from the datasets, allowing more precise peptide identifications.

In the first year of this research project, the critical analysis capabilities have been identified and developed to enable high-performance data analysis and identification of proteomics samples. In FY 2009, these tools will be placed in routine operation, and the capabilities will be demonstrated on biological samples.

Development of Gaming Technology for Cognitive Enhancement in Predictive Analytics

Roderick M. Riensche, Patrick R. Paulson, Gary R. Danielson, Scott Butner, Lyndsey Franklin,
Stephen D. Unwin, Nino Zuljevic

◆ This project aims to develop techniques and a systematic framework to enable the creation of a specific type of serious game; one in which users collaboratively and competitively explore and select plausible scenario outcomes generated using predictive computational models. ◆

As computational ability increases, models continue to become more complex, simulating an ever-increasing range of both physical and behavioral phenomena. Ultimately, it is the duty of the human consumers of these model outputs to reason over implications, to identify risks and opportunities, and to formulate and implement plans to capitalize on opportunities and mitigate risks. We seek to streamline this interface, allowing human players to maintain an interactive role in the modeling process, tapping their creativity and ingenuity to facilitate a better prediction of real-world behavior.

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 games, content delivery and interactions are designed to stimulate the user's senses to provide an engaging, memorable experience and enhance the user experience by augmenting cognitive functions such as memory, attention, processing speed, and cognitive control. Games also present a natural environment for problem-solving. In many games, success is achieved by repeatedly solving similar but non-identical problems; in others, players achieve success by solving a specific problem repeatedly by doing so more quickly and efficiently. Previous work has acknowledged this with the creation of serious games devised for the purpose of exploring possible decisions rather than a focus on training. These efforts have typically dealt with very specific problem domains.

We believe that a more generalized approach can add value by making game-based approaches more accessible in modeling and analysis problems. In our project, we seek to keep the computational modeling software separate from the game software. While not seeking to create a purely generic game engine that could be plugged in to an arbitrary computational model without modification, we are attempting to advance the state-of-the-art method in that direction by developing a methodology and framework to facilitate easier application of gaming approaches to model outputs.

Our progress during FY 2008 has been in three parallel efforts:

Development Environment. In order to facilitate experimentation with model interfaces, we first constructed a prototype development environment that involved the evaluation of both game and three-dimensional visualization engines. We decided on a hybrid approach using a three-dimensional engine that is not a full-fledged "game engine" but provides easy hooks to allow manipulation from the external code.

Methodology Definition. 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 the players and models. While the architecture does not prescribe any one gaming paradigm, it defines some key ingredients of a game configuration by which interactions between players and models are defined, including a set of each of the following: game parameters, domain models, roles, game elements, and handles (factors influenced by players). These are implemented in the prototype environment to provide an end-to-end flow of information between users (players) and data (model outputs).

Proof-of-Concept Implementation. During FY 2008, we set out to create a proof-of-concept game implementation that uses a computationally trivial model as a means of exercising our game configuration framework. We selected a simple economic profit model and constructed a scenario involving a housing market involving builders, bankers, speculators, and buyers. We then used our methodology to define a game configuration for a turn-based game that utilizes the outputs of an implementation of that model to drive behaviors of game elements. This is being implemented in a computerized prototype that demonstrates the basic functionality of the individual pieces.

Simultaneously, we are defining a game configuration for a more complex domain dealing with climate change, biofuels, and national resilience. Future efforts need to be focused on translating that configuration into a working implementation while refining our methodology and evaluating the effectiveness of the resulting game.

Development of Gaming Technology for Evaluation of Predictive and Adaptive Performance of Cyber Security Defense Systems

Louis M. Martucci

◆ This project focuses on the use of serious gaming technology to develop inherent insights gained from human gaming interactions in the arena of cyber security. Our approach is to employ a red-blue team concept in which players form teams to enact offensive or defensive roles with respect to a protected asset. This method implicitly captures the human creativity and unpredictability elements that other security assessment analytic methods often lack. ◆

While entertainment and training types of gaming in physical space are well-documented, there is scarce research available on the use of serious gaming to explore, test, and evaluate the efficacy of cyber security defense systems. Specifically, the serious game is being developed with the intent of evaluating predictive/adaptive attributes and/or to enhance security awareness offered by cyber defense systems either in existence or under development. The technical challenge of the current project is to translate the conventional gaming technique into cyber space, where dimensionalities and human engagement require different thinking, visualization, and performance within a serious game environment. We are building on prior project experience in generating a serious gaming application in physical (not virtual) space, wherein we pursued a red-blue team approach in assessing the vulnerability and penetrability of an actual physical facility.

The red-blue team concept is among the most proven and pragmatic of approaches for testing the efficacy and improvement potential of physical security safeguards. This approach captures the elements of human creativity and unpredictability that more analytic methods of security assessment lack. We propose to produce an innovative computer gaming environment that crosses this approach into the cyber arena, with an emphasis on power grid infrastructure supervisory control and data acquisition (SCADA) systems. Our goal is to make the red-blue team concept as valuable a tool in assessing and improving the efficacy, reliability, adaptability, and predictive attributes of cyber systems as it has proven to be for testing physical security systems.

Our supporting objectives are as follows:

- Develop specific hypotheses for the value of the cyber gaming/space concept that incorporate the performance metrics by which the concept can be measured.
- Develop the notion of cyber battle space in order to describe more definitively the arena wherein the envisioned serious game would be played.

In FY 2008, this project made substantial progress in 1) the development of a tabletop non-computerized game with well defined non-restrictive rules, and 2) initial development of the metaphorical cyber battle space concept. We created a SCADA/cyber security game that allows administrators to game various human or computer counterparts. Several experiments/game trials were conducted through progressive iterations of the tabletop game, which involved SCADA experts and our technical team. Each game was facilitated and represented by a game master from the project team who arbitrated the outcome of player actions. This process was effective in learning about SCADA systems and associated vulnerabilities from players who were infrastructure and cyber experts. Feedback from these experiments indicated that the players had gained insight into the prospective vulnerabilities of power grid science computing division and associated cyber systems.

Our second major thrust was in the development of cyber battle space, the arena where the serious game will be played. We defined the state space description to require two dimensions associated with each security asset: strength of residual safeguards and level of residual functionality. Safeguard strength is a metric of the combined effectiveness of the measures in place to protect the asset from an attacker; the level of functionality reflects the degree to which the asset is compromised by the attacker once the combined safeguards have been defeated. The status of each asset defines the system location with regard to two of the dimensions. When the functionalities and safeguards strengths are defined for all N assets in a system, then the system's location is determined with regard to all 2N state space dimensions. The basic development of the serious game technology and defining the fundamental state space description of cyber battle space were the most important findings of the current year's work.

Efforts in the future include developing a functional prototype serious game that will incorporate cyber security defense concepts in an applicable domain or in a SCADA power grid domain. Further, we need to continue development of the state-space idea that we initiated in FY 2008, including the supporting mathematical framework addressing asset functionalities and safeguard strengths. Our expectation is to create a new, innovative technical capability completely centered on serious gaming methodology to evaluate and enhance cyber defense systems and to expose vulnerabilities through the power of a red-blue team competitive modality.

Development of Petascale Algorithms for Molecular Modeling

Eric J. Bylaska, Karol Kowalski, Jarek Nieplocha, Tjerk P. Straatsma

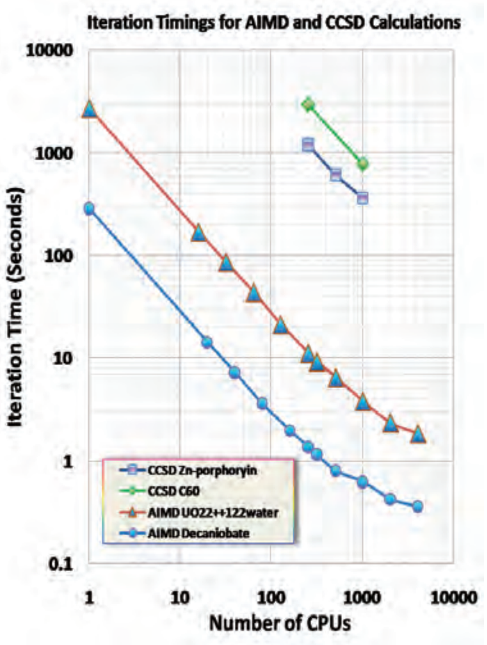
◆ Fundamental algorithm developments are needed to ensure that the most advanced simulation technology in computational chemistry is used at PNNL. The projected size of the next-generation supercomputers will be very large (100,000+ processors), suggesting that current simulation times and particle size limitations will be overcome in future years by brute-force increases in computer size. Computational chemistry methods being developed under this project will allow us to use the next generation of leadership-class supercomputers. ◆

Large-scale computers are evolving at such a rapid pace that the development of robust and high-performance molecular modeling tools requires that algorithms and implementations are tuned to the target computer system. However, even with the current successes of molecular modeling software on today's parallel computers, software remains limited in parallel scalability that will prevent its use on the next generation of petascale computers. Current molecular modeling software was designed and implemented for massively parallel computers that have a simple and homogeneous structure (i.e., single processor nodes with a homogeneous node-to-node communication pattern). Next-generation computers will have multiple core processors, multiple processor nodes, and hierarchical network fabrics and will have significant consequences for the design of next-generation scientific software.

The development and implementation of novel petascale algorithms for computation chemistry is the main goal of this project. Hartree-Fock, density functional theory, coupled cluster, and classical molecular dynamics theories will be targeted. We propose to investigate methods for latency hiding and data reorganization in the context of the chemistry algorithms pursued under this project. The goal is to improve scalability by removing data transfer costs from critical paths of the computations. All objectives involve methodology design, implementation of the resulting algorithm, and applications to representative problems. The developed algorithms will be tested and demonstrated on the leadership-class computers located at national laboratories at Oak Ridge, Lawrence Berkeley, and Pacific Northwest.

Significant progress has been made on several project tasks. A new parallel decomposition in the pseudo-potential plane-wave density functional theory program in NWChem was implemented. So was a new parallel decomposition in the band structure program in NWChem. A new parallel algorithm for implementing hybrid DFT was developed, and an algorithm was developed and implemented to compute the four-index transformations used in coupled-cluster theories. In addition, a task-level parallelization for all of the modules in the NWChem computational chemistry package was developed, state-of-the-art open-shell coupled-cluster calculations of hydro-carbon polarizabilities and nanoparticles stabilities were performed, and extensive tuning and validations of the newly developed algorithms were performed. Five publications and one manuscript in publication resulted from this work.

A highlight of FY 2008 was our work on the validating and tuning of the plane-wave density functional theory and coupled cluster theory programs in NWChem on the supercomputers at NERSC, ANL, and PNNL. Our programs have been demonstrated to scale to 1,000-10,000 CPUs, which is a significant achievement since very few density functional theory and ab initio theory programs are known to scale beyond a few hundred CPUs. However, the goal of our developments has been not only to have standard density functional theory and ab initio theory programs able to exploit the full power of emerging machines efficiently to allow the treatment of much larger systems and domains, but also to be able to treat problems with a large but not excessive number of atoms. This allows us to solve relevant problems more quickly as opposed to solving large problems in a scalable manner. Example benchmark timings are shown in the figure for these two programs for modest problem sizes, at which both programs have been demonstrated to scale to ~10,000 CPUs. These significant improvements in parallel scaling now allow us to perform simulations that used to take weeks and months in hours and days.



Timings on NERSC Franklin computer system for various ab initio molecular dynamics using the plane-wave density functional theory program and coupled cluster calculations or modest problem sizes.

Discovery of a Biomarker Signature in Response to Nanoparticle Exposure

Katrina M. Waters, Somnath Bandyopadhyay, Norman J. Karin, Brian D. Thrall

◆ This project will use high-throughput genomic and proteomic technologies to identify size-dependent biosignatures of inflammation associated with inhalation exposure to engineered nanomaterials. Subsequently, a validated set of biomarkers selected from the biosignature could be used for the evaluation of human response to nanoparticulates using minimally invasive techniques. ◆

There is a growing awareness by the public and scientific community that an understanding of the potential toxicity of engineered nanomaterials is needed to guide science, technology, and regulations in a manner that ensures human and ecological health. The mode of action for particulate matter-induced inflammation in the lung has been well-established for micrometer-sized particles. For nanoparticles (<100 nm), it is unknown but hypothesized to be different because these particles look more like viruses than bacteria to lung epithelial cells. Under this project, we are developing a strategy to understand the characteristics of engineered nanomaterials that lead to early indicators of respiratory damage or disease.

This project uses microarray technology and integration of genomics and proteomics data sets to identify a size-dependent biosignature of nanoparticle-induced lung inflammation through three project phases: 1) microarray and proteomic data from lung tissue of mouse models of inflammation as preliminary data sets to develop bioinformatic capabilities, 2) microarray analysis of mouse macrophage cells from an in vitro model exposed to a range of particle types and sizes to identify genes that distinguish composition and size-dependent particle-induced responses and to identify the appropriate particle sizes to test in vivo, and 3) microarray analysis of lung tissue from mice exposed by inhalation to a range of particle sizes and types to confirm the in vivo response to nanoparticles.

In FY 2007, we analyzed the microarray data for in vitro studies, specifically focusing on type- and size-dependent signatures of response and compared these signatures to previously collected microarray data from lungs of mice exposed by inhalation to micron- and nano-sized particulates. Biological pathway and transcription factor binding site analyses identified unique modes of action for particulate- and LPS-induced inflammation. In contrast, the modes of action across multiple size classes of amorphous silica were virtually identical. Proteomic analysis of the secreted effectors in the media of nanoparticle-treated macrophages confirmed the induction of several inflammatory cytokines identified in the microarray study. Regression analyses of the gene biosignatures with surface area dose metrics revealed unique gene sets that were highly correlated with low dose response and high dose response profiles, demonstrating dose-dependent regulation of distinct cellular processes.

Statistical classification of our microarray and proteomic data sets revealed some interesting patterns. First, we were able to perfectly distinguish LPS- from particle-induced inflammation using the microarray data, but not distinguish different particle classes from each other. Using the proteomic data, however, we were able to identify select peptide biosignatures that represent distinct cell activation pathways for different nanomaterial classes. When we integrated these data on a feature level, we were able to achieve almost perfect prediction of particle class, vastly improved over either data type in isolation.

During FY 2008, we confirmed dose-dependent regulation for several genes using real-time reverse transcriptase polymerase chain reaction on parallel study samples. We also completed a full time-course macrophage experiment this year using surface area equivalent doses of two different amorphous silica particle sizes. The data from this study demonstrated time-dependent regulation of many biological processes involved in the apoptotic cell death of macrophage cells from nanoparticle treatment. We were able to determine early gene expression indicative of regulatory processes and late gene expression indicative of irreversible cell death. This study provided us with many new processes for biosignature development.

We also compared the gene expression changes from the macrophage cells with that seen in mice exposed to a variety of different nanomaterials. During the past year, our discussions with investigators from the National Institute for Occupational Safety and Health allowed us to receive lung tissues from mice exposed to several relevant particulates (carbon black, asbestos, and carbon nanotubes). We performed microarray analyses on the lung tissues from this study and identified tissue-level particulate matter-induced inflammatory pathways. Strikingly, the mice treated with single-walled carbon nanotubes demonstrated the most significant inflammation and tissue damage in the study, more so than asbestos or carbon black particles. The microarray signatures are consistent with this finding, as the carbon nanotube-exposed lungs contained the most number and highest magnitude of gene changes over the other treatment groups. These data have enabled us to determine conserved biosignatures between cultured macrophage cells and lung tissue exposed to manufactured nanomaterials.

Dynamic Scenarios for Organizations in Infrastructures

Paul D. Whitney, Sandra E. Thompson, Katherine E. Wolf, Garill A. Coles,
Jonathan Young, Cindy L. Henderson, Bonnie L. Hoopes, David A. Niesen

◆ Government-wide decision-makers routinely estimate the likelihood of future events. Currently, predictive processes are dependent on an individual's judgment, experience, and instinct prior to selecting a course of action in response to a set of circumstances. We will exercise two widely disparate modeling methodologies to support the tasks integrated with relevant associated data and evidence to present decision-makers with predictive likelihood estimates. ◆

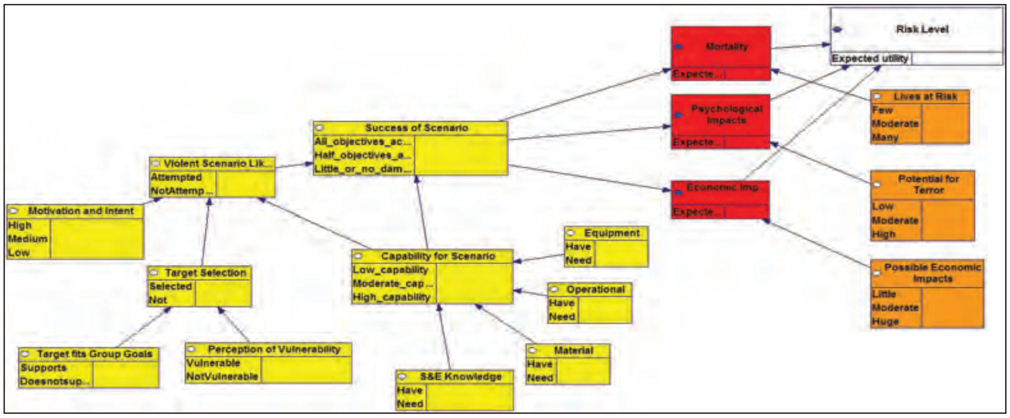
This project will develop predictive modeling advances focused on two modeling/prediction methodologies at extremes in mathematical complexity. The less complex of the two is judgmental bootstrapping forecasts, which are statistical summaries of well-structured expert elicitation; the more mathematically complex is dynamic Bayesian network models. The former has the benefit of being directly transparent to individuals with a variety of technical backgrounds; the latter provides more generalized quantitative modeling capability with established methods for integrating data.

Specific technical advances on which this project focuses are the integration of information from the two modeling approaches and the associated data and evidence. Models for the technical and social components will likely be known with differing accuracies; a critical challenge is linking across these model domains while respecting this fundamental difference in certainty level. In recognition of the rapidly evolving state of computational predictive social modeling, a major focus is methods for validating and understanding information in the combined models and data.

In FY 2008, we demonstrated how the Bayes net approach for techno-social modeling can successfully combine social and technical models and perform data integration. We engaged subject matter experts with knowledge of intelligence community requirements and explored multiple model options related to nuclear proliferation and terrorist threats (specifically, improvised explosive devices [IEDs]). We developed representations and linkages between behavior and process (technical) models, IED scenarios, and inferences and examples. We focused on infrastructure and IEDs based on PNNL's expertise in the analysis of IED threats; specifically, that IEDs represent simple attacks and that from a social/behavioral perspective, IEDs as an attack tool include numerous motivational elements challenging to model. We constructed a model designed to represent generic threats (meaning that elements within the model are relevant to IEDs but are also to other forms of terrorist activities or bad-actors). The general ingredients of a scenario and examples include who (insurgency, religious, or political extremists), what (explosive materials), where (geographic location), when (date/time, perhaps with a preceding observational event), why (the desired outcome), and how (the method of attack execution).

Our general threat model is designed to encompass a wide range of threats beyond terrorist activities. The model computes relative risk across scenarios based on currently available information and predicts scenario occurrences. Two dynamic variants of the generic model were developed and contrasted. Given sufficient drive and motivation, a group will find its way to the appropriate capability necessary to achieve group goals. With this approach, threat level increases over time. The second dynamic variant of the generic model (not depicted) includes a group with the drive and skill to increase capability and an opponent with the ability to increase protection level. The outcome depends on the interaction between these competing drives.

The team is exploring the feasibility of layering the generic model over an IC-vetted IED development process to begin validating that the model performs as expected. A critical area for future research is developing and demonstrating validation strategies for each model across disparate threat and attack vectors.



Left-hand side boxes are critical concepts for understanding threats. The middle shaded (dark) boxes represent risk, and the lower three right-hand side boxes represent consequence. Technical aspects in the model are represented in capabilities and in the consequence parts of the models. Social aspects are captured in motivation, intent, and target selection nodes.

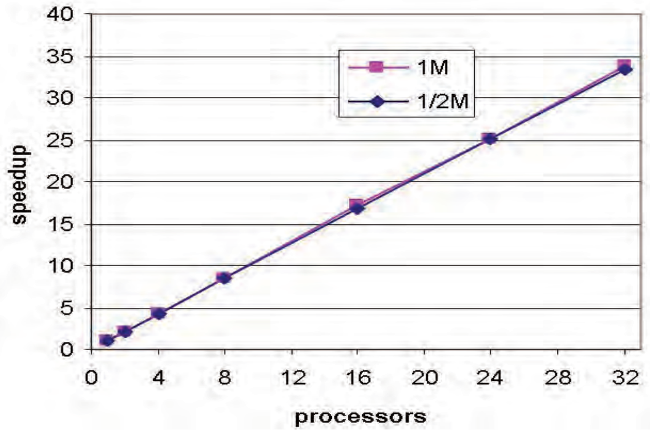
Evaluating Multithreaded Architectures for Irregular Data Intensive Applications

Andrés Márquez

◆ Applications important to research in computational biology, power grid analysis and management, materials science research and development, cyber security, and related scientific fields do not work well on traditional cache-based architectures. This project evaluates the potential for applying emerging multithreaded computing architectures to irregular data-intensive applications because multithreading has the potential to address the bottlenecks inherent in cache-based architectures. ◆

Under this project, a feasibility study was conducted to determine if important scientific applications currently running on other machines can be successfully ported to multithreaded architectures and attain significant performance gains with very high processor use. Data-intensive algorithms with irregular behavior are expected to show absolute speedups not attainable on conventional architectures that suffer increasingly from serious memory bottlenecks. Multithreaded graph and sparse numerical algorithms developed at PNNL that exhibit poor locality of reference and consequently poor cache performance were evaluated. As a point of comparison, a regular multithreaded application was also examined. As target architectures for experiments, the novel Cray XMT and Nvidia QuadroPlex GPGPU were selected.

At the end of FY 2007, the first experimental research Cray XMT machine, a third-generation multithreaded system, on the PNNL campus, was deployed. The XMT infrastructure is based on the Cray XT3/4 platform, including its high-speed interconnect and network topology as well as service and input/output nodes. The difference is that the compute nodes of the XMT use a configuration based on four multithreaded Threadstorm processors instead of four AMD Opteron processors. The XMT system enables the execution of applications built entirely for the Threadstorm processors in a similar manner as the MTA-2 as well as the execution of hybrid applications, in which portions of the application execute on either the Threadstorm or mainstream AMD Opteron processors.



Performance speedup curves for in- and out-of-core implementation.

During FY 2008, an extended set of application benchmarks and performed measurements were ported on the new set of multithreaded machines (with emphasis on the Cray XMT), optimized benchmarks for maximum performance and scalability, and published the findings. Using data-driven application system paradigm, multi-threaded architectures with uniform memory access allowed sophisticated analysis to identify relationships and patterns in network traffic. Using algorithms based on graph theory against streaming network traffic data to identify relationships and patterns within the traffic flow in real time will help address the problem set by identifying exploits and vulnerabilities as they are developing and predict when and where future attacks may occur. The computing power of novel architectures will allow for reduction of terabytes of data in a relatively small mesh or graph yet maintain real-time situational awareness for enterprise network.

Building on experience gained in previous project phases, parallel multithreaded code for sparse storage and query of categorical joint-distribution data were refactored. This application finds use in network traffic analysis. The adaptation to the Cray XMT addresses two new challenges, namely out-of-core processing and fast Lustre global shared file access. The last two changes generalize the problem statement to the data-intensive case. The outcome of this study shows the out-of-core implementation underperforming only slightly its in-core counterpart. This data constitutes one of the first out-of-core XMT evaluations published so far.

An initial port of a latent Dirichilet clustering algorithm was created. Applied to text analysis, this algorithm provides a generative probability model for a set of topics derived from documents and associated word occurrences. The implementation on the XMT investigates the use of table lookups under a constrained numerical dynamic range to reduce arithmetic intensity. Continued work on this algorithm will be performed under programmatic funding.

A regular multithreaded application ported on a Nvidia QuadroPlex GPGPU was investigated: a gridless application Smooth Particle Hydrodynamics Fortran90 program with an explicit Lagrangian formulation. The code uses Verlet integration. Mapping the two most intensive subroutines on the QuadroPlex yields a speedup of 20 times over a state-of-the-art single-threaded processor.

Fundamental Investigations of Heterogeneous Catalysis Using Computational Methods

Donghai Mei

◆ This project aims to enhance the applications of revolutionary and revolutionary 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, energy carriers, and energy conversions. The challenge is to understand how to design new catalyst structures to control the activity and selectivity of the specific catalytic process, hence the importance of developing new theoretical methods, algorithms, and software for high-performance computers to enable understanding of the fundamental behavior of chemical reactions over various catalyst surfaces on multiscale levels. Effectively combining quantum chemistry computational methods for the electronic structures and statistical thermodynamic and dynamical theories for individual reaction steps will enable kinetic modeling to bridge gaps in temporal and spatial scales that separate elementary molecular reaction processes from the statistical behavior that governs chemical reaction kinetics at the macroscopic scale. As a result, two computational modules, first-principles-based kinetic Monte Carlo (KMC) simulation and adaptive KMC simulation, have been developed under this project.

Hydrogen is considered one of the most promising energy alternatives due to the limited supply of and environmental concerns related to fossil fuel use. Hydrogen is largely produced by steam reforming of hydrocarbons and alcohols that contain a trace amount of carbon monoxide to be removed by water-gas shift reaction and preferential oxidation before it can be fed into proton-exchange membrane fuel cells widely used in mobile instruments and vehicles.

During FY 2008, we studied the reaction kinetics of water-gas shift on three low-index single crystal copper surfaces using first-principles-based KMC simulation. First, we calculated the adsorption energies of all reactive surface intermediates as well as the reaction energies and activation barriers of key reaction steps using first-principles density functional theory (DFT). These DFT-based intrinsic kinetic parameters were used as input in generic first-principles-based KMC simulations. We found that the associate reaction mechanism through carboxyl surface intermediate (rather than the redox reaction mechanism) assumed in previous study is the dominant reaction pathway in water-gas shift reaction on copper catalyst surfaces.

Also during FY 2008, we developed an adaptive KMC simulation module in collaboration with Graeme Henkelman's group at the University of Texas at Austin. It can be used to identify different elementary reaction paths without chemical intuitions; provides an efficient computational method for discovery of complicated reaction mechanisms; and simulates reaction kinetics and long-time surface dynamics for heterogeneous catalysis: methanol decomposition on Cu(110) and Cu(100) surfaces and the reactivity of formate on Cu(111). For example, the potential energy surface of methanol decomposition on Cu(110) has to be mapped in an unbiased way. For each step in methanol decomposition into CO and hydrogen via one of three possible (O–H, C–H, and C–O) bond scissions, multiple reaction pathways are identified. Starting from the stable adsorbed methanol on Cu(110) that used as the initial (reactant) state, the transition (saddle point) state, and the final (product) state of each reaction or diffusion is determined without knowledge of final state. In other words, reaction and diffusion paths are determined without chemical intuition. The pre-exponential factor of each reaction is obtained by vibrational frequency calculations of every state. Therefore, within the harmonic transition state theory frame, reaction rate of each identified pathway in the reaction network is obtained. Our calculations agree with prior observations and results.

BaO supported on γ-Al_2O_3 has attracted significant attention due to its potential application as an NO_x storage material used to treat exhaust emissions of internal combustion engines operating under lean (oxygen rich) conditions. Numerous studies (both experimental and theoretical) have focused on the elucidation of the interaction of NO_2 with BaO and the identification and characterization of NO_x species (nitrites and nitrates) formed on the BaO storage material as well as γ-Al_2O_3 support. However, the special role between the active catalytic BaO phase and γ-Al_2O_3 support in determining properties of practical BaO/ γ-Al_2O_3 catalysts remains poorly understood. During FY 2008, we studied the morphology of BaO on γ-Al_2O_3 surfaces under different BaO loading conditions. An amorphous BaO overlayer would be formed under high BaO coverage, while small BaO clusters is preferred under low coverage. The aggregation process is determined by initial BaO adsorption sites and surface hydroxyl groups. We calculated the adsorption energies and vibrational frequencies of NO_x on the γ-Al_2O_3-supported BaO monomers and dimers. Combined with experimental results of infrared spectroscopy, we identified that the nature of both the surface and bulk types of nitrates on the NO_x/ BaO/ γ-Al_2O_3 storage system. In FY 2009, we anticipate that this concerted effort that combined experimental and theoretical study will continue and strengthen our capabilities of the catalysis research program at PNNL.

High Performance Data Analysis Pipeline for Online Smart Mass Spectrometry

Navdeep Jaitly, Anuj R. Shah, Andrei V. Liyu, Yan Shi, Ashoka D. Polpitiya, Joshua N. Adkins

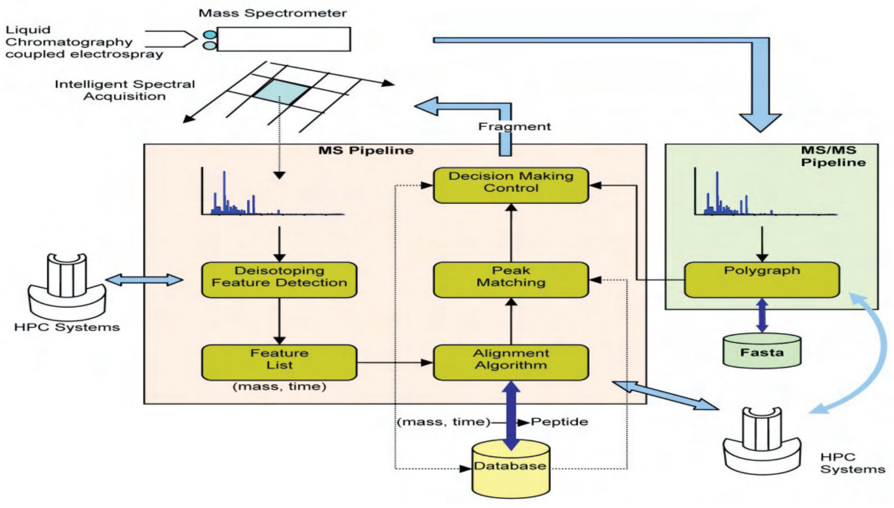
◆ Data collection and analysis from multiple sensors generally result in an over-collection of prominent data items, while underrepresented items may be ignored or missed. We are developing an online analysis pipeline to control sensors in an automated manner to maximize the information content generated 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 the prominent data features in large-scale studies over what should be achievable through intelligent, online acquisition of such data. 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 propose to 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 the use of pre-existing knowledge to optimize the dynamic collection of events. Through the use of this system, we aim potentially to reduce the number of analyses required in constructing a comprehensive detection database from thousands of possible experiments (each with over 10,000 detection events) to only tens. In addition, the computational system we develop will provide an order-of-magnitude improvement in the 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.

In FY 2008, we made significant progress in the identification and development of the individual processing modules of the overall analysis pipeline. Brief descriptions of specific areas in which improvement has been made follow.

- Data acquisition software modules have been written for the mass spectrometer, and individual COM objects have been tested.
- The middleware for data-intensive computing integration (MeDICi) integration framework has been incorporated within the application to manage the data transfer and processing activities between the instrument and the individual processing components.
- The de-isotoping algorithm has been modified to work online in real time (i.e., on an incoming data stream from the instrument) as opposed to offline in which all available data were collected prior to processing or analysis.
- A small-scale scheduling program was written to allow for the possibility of connecting multiple instances of the de-isotoping algorithm in the pipeline. This accomplishment also 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 the users of the system.
- The central visualization and control software is in development. Current functionalities include visualizations for data received from the mass spectrometer as well as visualization for the results of the de-isotoping process.

Among project goals for FY 2009 are to apply the serial version of algorithm to the biological communities' sample of a proof-of-concept for optimized database development and develop a theoretic algorithm for optimal decision-making during the course of an experiment, including choosing ions, determining the type of fragmentation, and augmenting databases with MS/MS identification.



High-performance data analysis pipeline for intelligent mass spectrometry.

Hybrid Computing Solutions Applied to Feature Extraction, Characterization, Classification, and Clustering

Harold E. Trease, Robert M. Farber, Adam S. Wynne

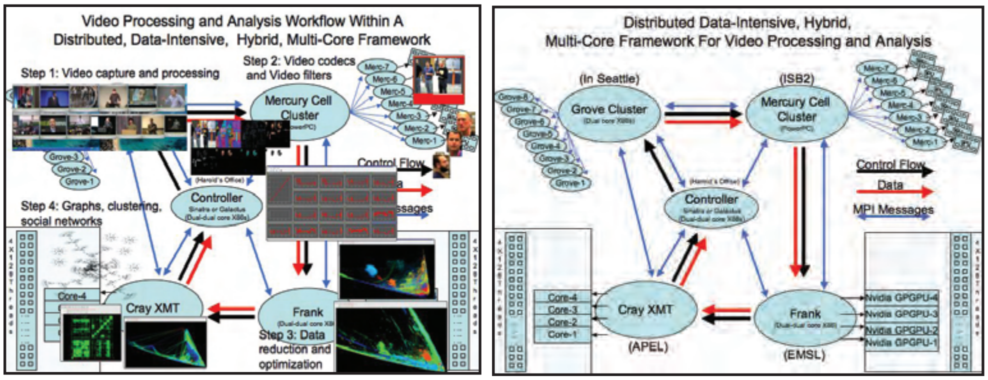
◆ With the inability of the computer industry to keep pace with Moore's Law scaling of computer chip clock speed, power dissipation rates, and communication bandwidth requirements, our whole computing infrastructure is being disrupted with a trend toward multicore computing hardware platforms. New algorithms, 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 is increasing for applications ranging from surveillance camera networks to 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 surveillance sources (i.e., 100s to 10,000s+) or how to store and analyze massive archived databases. Without automated, high-throughput analysis tools, most captured video data may be stored and archived but may never be analyzed or processed, except in forensic contexts where a critical event occurs that requires specific segments of video to be examined.

In this project, 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. The major workflow steps involved in processing unstructured data include:
1) importing and ingesting data,
2) running information processing algorithms to generate signatures,
3) performing principal component analysis (PCA) dimensionality reduction on the signatures, and
4) generating/performing graph analysis to extract relationships.
The MeDICi architecture will be used to manage workflow across the different hybrid computing platforms. The results of this project will 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 large, sparse graphs to discover data 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: 1) a control network that directs the workflow, 2) a flow network that communicates data, and 3) a point-to-point message communication network for both functions and data. All network nodes are distributed across geographic locations, thus making the Internet communication bandwidth a critical component. The controller, Cell, and Nvidia GPGPU clusters reside at the main PNNL campus in Richland, Washington, while the Grove Linux Cluster resides at PNNL's Seattle office.

The major results of this project include the successful mapping of a complex workflow for video analysis onto a hybrid, multicore computing platform, achieving near linear scaling in performance for several of the individual pipeline steps (particularly the PCA on the Nvidia processors), an initial mapping of the video workflow using a pipelined MeDICi implementation, and publishing several papers and making conference presentations that describe in detail the implementation and performance/scaling results for this



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 data flow network manages raw and processed video data flow throughout the network, and 4) a communication network manages the messages passed between the network (master) nodes and cluster (slave) nodes, where message may contain both data and functions.

Information Physics Methods and Applications

Joseph S. Oliveira, Dean W. Gull, Janet B. Jones-Oliveira

◆ This project is developing a computational framework to break down existing barriers of scale in the analysis of seemingly disparate information to identify actionable intelligence. It will equip users with powerful tools to tackle critical analysis challenges in nonproliferation, homeland security, and national defense. Construction of a prototype will advance scientific knowledge in the application of scale-free information physics methods required by the national security and intelligence communities and the greater scientific community. ◆

The user community is flooded with massive quantities of mixed data through which they must search for the few tidbits of information relevant to the crisis-of-the-day. The integration of diverse channels defines a complex network-of-networks model for which mathematical and computational tools analyze and fuse multiscale data. The Integrated Decision-Making system will generate a model for the analysis of disparate time-independent signals of multisource data that includes visual, acoustical, and lexical data types. Applied research into information physics, multiscale classified supercomputing, and scientific visualization will make possible a working integrated decision-making system prototype. This computational framework will break down the existing scale barriers associated with the analysis of seemingly disparate information to identify key information. The process of constructing this prototype will advance scientific knowledge in the application of scale-free information physics methods required by the greater scientific communities.

In FY 2008, the focus of this effort was to obtain and qualitatively and quantitatively analyze data from various problem domains to demonstrate the analytic utility of the MICAH framework. To this end, we successfully obtained several data sets corresponding to Internet traffic, decompiled software binaries, and other timely network structures. The Internet traffic network has been extensively analyzed using the MICAH, where the qualitative, unique, minimal cycle analysis identifies a clustering of IP addresses actively engaged in bi-directional communication. Comparing the quantitative minimal cycle distributions over the time scale of days quickly identified anomalous Internet behaviors like port scans.

In addition to the aforementioned MICAH analyses, two tasks were addressed. The first research area involved finding optimal pathways for undeveloped terrain traversal. Preliminary results demonstrate that real-world data on the order of hundreds of kilometers squared may be analyzed effectively for optimal pathways within a matter of minutes. The second research problem was to identify a mathematical framework for integrating and analyzing heterogeneous relationships defined between mixed data sets. A novel approach to this problem is briefly outlined below, but the complete solution and implementation is beyond the scope of this research. If we consider the direct union of all of the heterogeneous datasets to form the partially ordered ground set upon which several (independent) relations will be defined for a given relationally well-defined context, then one canonical representation for this partially ordered direct sum structure may be obtained as an indexed family multi-cubes (multi-signed sets ordered by opposite component-wise inclusion). It has been established that multi-cubes and their associated face lattices possess a rich combinatorial algebraic geometric-topological structure. Evidently, the relational algebra structure of this family of lattices can be extended to obtain a new class of "involutory concept lattice-like" objects that admits a model of MV-algebraic logic realized by a set of equations. Also, each MV equation is in fact a model in some modal universe of contextually defined object classes and attributes by construction: a logical system of belief that has as valuations "yes, no, and to be determined." Quantum event logics are good examples of modal belief systems similar to those defined by multi-cubic lattices. Relationally dependencies between heterogeneous data sets can be tested using models of MV-equational logic defined from multi-cubic lattice representation of heterogeneous data sets.

We next observe that every multi-cube (multi-cubic lattice) may be identified with both a hypergraph of relational dependencies and an associated matroid/polymatroid. From this realization, it follows that a multi-cube of heterogeneous data sets can be used to obtain a hypergraph-matroid representation that presents a context in which multiple relational queries can be made of the multi-cube of heterogeneous data sets. It also follows that these new structures define a class of mutivalued cubic concept lattices where each relation defined on this dataset-of-datasets will generate a partition of the ground multi-cubic lattice. The partitioning of this ground partially ordered set in turn gives rise to a partition lattice, wherein each atomic element of the lattice will correspond uniquely to the partition induced by a single data relation. The join of atomic elements thusly corresponds with partition refinements. We therefore have that each element in the partition lattice will allow the analyst to explore the corresponding partition refinement, which in turn will define a weighted data cluster. We will address the problem of testing the validity of a compound hypothesis whose domain of discourse ranges over disjointed sets or classes of object-attribute data.

Intelligent Compression and Data Organization for Multidimensional Data Volumes

Nathaniel Beagley, Chad Scherrer, Yan Shi, Brian H. Clowers

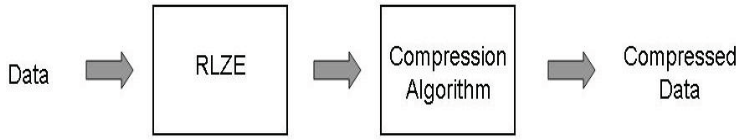
◆ A significant challenge in creating and analyzing the large data sets generated by scientific experiments is how to store the raw data and access its pieces to perform an analysis task. This research is targeted at enhancing the scientific discovery process through efficient data management and access specifically by improving storage and analysis utilizing compressed data files. ◆

Experiments that produce massive quantities of data face challenges in storing the raw data files and providing fast, on-demand access to information from the data that would allow for efficient analysis. The analysis domains generally have two characteristics: there is reluctance to discard raw files at the risk of permanently losing information, and the analysis requires extraction of discrete small pieces (or segments) of the larger data volume. Comparing features across multiple samples is a good example of the second characteristic. For each feature, the data segment characterizing that feature needs to be extracted from each sample data file, which in the case of ion mobility spectrometry (IMS) data could potentially be hundreds of samples. Another illustration is any analysis algorithm that requires multiple passes through the data set; for example, the "shotgun metabolomic" analysis, where a first pass is made to find all compounds in a sample, requires a second pass to characterize each identified compound.

The problem with creating and analyzing large quantities of experimental data is how to store the raw data and access its pieces for an analysis task. Often, the strategy is not to store all the data or limit extracted features from the data, which can lead to repeating expensive experiments. When this strategy is not acceptable, the common solution is to store the data in a compressed form, which decreases both the storage space needed and the time needed to write the data to disk. However, this approach creates an additional problem in that accessing the data becomes cumbersome, leading to a decreased efficiency in many analysis tasks. This project creates an indexed compression scheme that allows the extraction of segments of uncompressed data from a compressed file without having to perform decompression the entire file. The benefits of storing data in compressed form are achieved and, at the same time, a method for easy, direct access to the compressed data files is provided. Any routine analysis that requires more than a single pass through the data files is thus accelerated.

During FY 2008, we designed, implemented, tested, and optimized an indexed compression scheme for our preliminary test data set, the IMS data stream. This is a data-intensive application area with an instrument-producing data on the order of hundreds of megabytes per second that must be stored without any loss of data resolution. Additionally, the instrument has close to a 100% 24-hour duty cycle, potentially producing terabytes of data over a year. Our storage solution had to be both computationally efficient to allow compression and storage in close to real time and provide a generous reduction in data file size to reduce as much as possible the load on the data storage infrastructure.

Multiple compression algorithms and strategies were tested, evaluating each 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 performs a run-length zero encoding algorithm (RLZE) over the data followed by compression via the LZF algorithm. RLZE is a custom adaptation of the common run length encoding algorithm that is both fast and optimizes compression size, utilizing the characteristic that the IMS data contains a large number of zeros. LZF is an established compression algorithm chosen for its speed, which achieves compression sizes similar to GZIP, the industry standard. The two algorithms applied in succession achieve a computation time able to keep pace with the rate of data production and generates optimized compression, providing a 99% reduction in data size over the instrument-produced raw data and a 60% reduction above the status quo data storage format. In addition, compressed data are stored in an indexed manner that allows direct, instant extraction of uncompressed data segments.



A compression methodology optimized for the IMS data stream.

Our algorithms are in the process of being integrated into EMSL real time; data capture and analysis environment for IMS is being implemented. This large-scale real world testing will measure the full increase in efficiency possible by using indexed compression methods. We plan to build on this initial success with the IMS data, and in FY 2009 build a set of generalized methods that can be applied to any type of data files. The resulting tool has the potential to save significant amounts of both money and time in data storage, access, and analysis over a wide range of scientific applications.

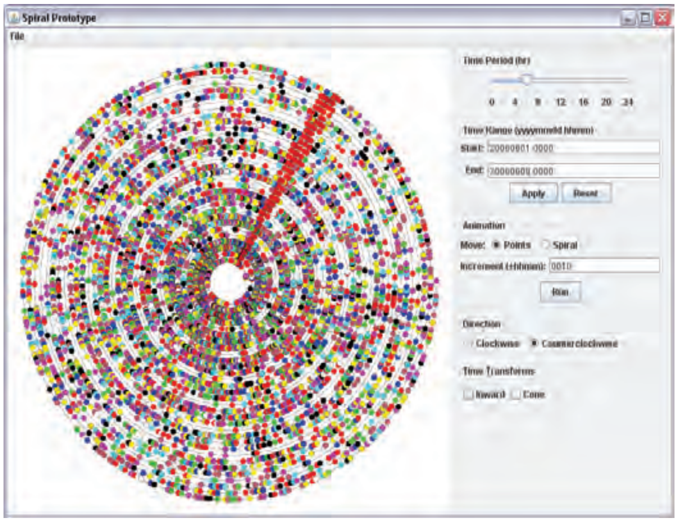
Interactive Visual Content Analysis of Real-Time Data Streams

George Chin, Natalie A. Freeman-Cadoret, Vidhya Gurumoorthi, Grant C. Nakamura

◆ As real-time problem solvers and decision makers, scientists and analysts need to be able to comprehend and act efficiently and effectively on the meaning and context of streaming heterogeneous data. To facilitate human understanding and comprehension of high-volume, real-time data, this project will develop and provide 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 to static data. Real-time data are dynamic, transient, temporal, and are created in massive volumes. Effective visualizations must be able to accommodate this dynamic behavior as well as abstract and present it in ways that make sense to 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 visualization or analysis tools.

A diversity of effective traditional visualization techniques already exists for the analysis of static data. A variety of techniques for visualizing time-dependent data have also been developed and studied. An aspect of our visualization 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.



Dynamic spiral timeline showing a periodic pattern in dynamic 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 scientists and analysts and connect to high-volume, real-time data streams to provide immediate visual analysis support. The visualization 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.

During FY 2008, we conducted requirements-gathering and analysis workshops with PNNL scientists and analysts who have real-time visualization needs. The domain areas that were the subjects of our requirements analysis included cyber security, computer networks and security, counterintelligence, supercomputing, and ion mass spectroscopy, applied mathematics, biological sciences, and national security. We collected and analyzed different kinds of real-time data from collaborating scientists and analysts and from other open sources. From our analyses of potential users and data sets, we identified three critical properties of real-time data that were most frequently analyzed. We characterized these properties as hierarchical, temporal, and relational patterns.

The main contribution of the project for FY 2008 is the design and development of dynamic visualization prototypes: the dynamic spiral timeline allows scientists to identify periodic temporal patterns; the Dynamic TreeView and TreeMap let scientists map dynamic data to hierarchies, taxonomies, and categories; and the Dynamic GraphView allows scientists to view transitions in the structures and relationships of changing data. Achieving rapid and efficient human cognition is a critical objective of these visualization tools as they instantly connect to the user's mental model of the problem, the data, and the data's changing behavior. These prototypes fulfill the project's goal of developing innovative visualization tools that will facilitate immediate comprehension and rapid visual analysis of dynamic data.

Knowledge Encapsulation Framework

Andrew J. Cowell, Michelle L. Gregory, Patrick R. Paulson

◆ 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 they already have (through semantic linkages and visualization) and discover related information from both traditional media (news, academic literature) and social media (blogs, forums). ◆

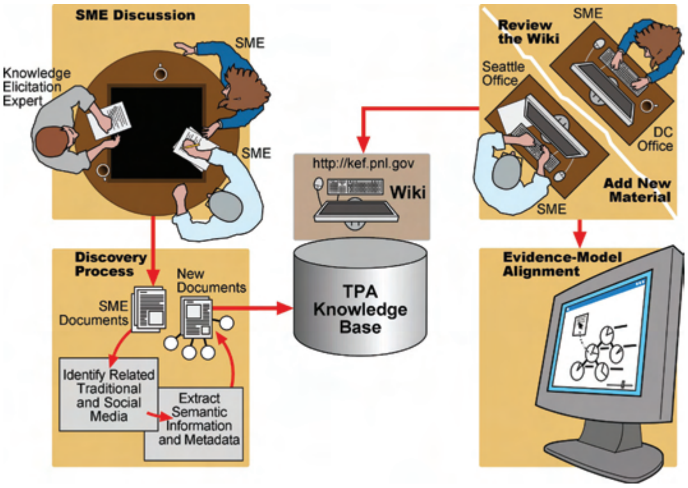
A knowledge encapsulation framework is designed as a knowledge ingest component supplying modelers (subject matter experts) with a means of compiling and therefore understanding journal articles, government reports, and other technical documents in order to design models and parameterize their inputs. More generically, it aims to comprehend the underlying structure of a document corpus, including elements such as major concepts, topics, named entities (people, places, things), sentiment (how people feel about a certain topic), and rhetoric (what people are saying, to whom, and for what reason). This project allows content to be presented in a variety of ways, but it allows us to populate a search strategy for finding new potentially related material. This project also is providing a knowledge reference for the models to promote model transparency through formal definition on model inputs and outputs as well as through structured descriptions of social science theories employed by the modeling teams.

Several aspects of this work are novel. Traditional collaborative problem-solving environments, expert systems, new Web 2.0 information stores, and even the new class of digital Aristotles (such as Project Halo) all share at least part of the vision. One aspect that makes this research unique is the way the annotation burden has been shared between extraction technology and the subject matter expert. Instead of leaving the task to identify topics and named entities to the subject matter expert (through tagging or keywords), a number of extractors perform first-stage annotation as documents are introduced to this framework. Another unique aspect is the automated discovery mechanisms that aim to grow the corpus of available documents by finding related material across both traditional and social media. This allows subject matter experts to be more confident in their model designs and parameterization, as they have more evidence on which to rely.

Through structured interviews (such as the Delphi method) with subject matter experts, we are able to construct formal representations of concepts of interest. In addition to material provided by the subject matter experts, these serve as a search description for this framework to find new related material along with the supplied material into the KEF knowledge base. The user can access this repository of information through the knowledge encapsulation framework wiki—a collaborative environment that allows users to see summary views of the data and discover new linkages.

We constructed each of the major knowledge encapsulation framework components and tested them to ensure that they were capable of supporting the vision. We used an open-source wiki engine (MediaWiki, the same used by Wikipedia and Intellipedia) with third-party extensions (such as Google Maps, plus a semantic extension that allowed us to define relationships within document text) to develop our collaborative environment. Discussions with our focus groups presented us with three distinct document collections that have served as test data. From these collections, discovery mechanisms have been developed to harvest material from the web to insert along side the collections.

As soon as a document is added, a sequence of operations built as a linguistic pipeline is applied to annotate the document. This pipeline consists of three main information types: a named entity recognizer, a summarizer, and a georeference component. The named entity recognizer is based on Connexor software that identifies proper names, selects common nouns, and maps them to semantic tags via their identified categories. Connexor Metadata is used to identify their names, categories, and lemmatized form. Based on publicly available MEAD information, the summarizer creates one or more pages of a source document by identifying the most significant sentences. It is used in the current pipeline to create summary properties for single-document



The KEF collaborative information analysis process.

pages. Finally, the geo-reference component provides a map view of source documents based on named entity recognizer locations that are checked against the Google Geocoding Service to create a set of coordinates associated with an article. For pages with multiple location names, these coordinates can be restricted to those that occur either most frequently or in the summary or title of the page to highlight the most relevant locations. After a set of pages has been processed, a new page is created with the map view using the Google Maps MediaWiki extension. This component creates a Geographically Aligned View page in the wiki.

There are a number of challenges in identifying information accurately through the named entity recognizer process. In FY 2008, we explored the best methods to handle co-reference resolution within and across documents as well as aliases. Additionally, accuracy of the models requires that information is correctly associated with time expressions. We also explored a solution to these areas and plan to integrate related technologies in FY 2009. In addition, the majority of the discovery process for new documents is currently manual. We intend to automate this process as much as possible to provide a more compelling user experience. Finally, the last phase includes the user aligning evidence identified in the documents with model descriptions currently not implemented.

We investigated a number of techniques that would allow us to create an interactive environment to mark documents and document elements (paragraphs, sentences, and statements) as being relevant or irrelevant to their study. Depending on model type, they may also describe the evidential strength and credibility before aligning the evidence to a node in the model. In FY 2009, we will implement this through a process of embedding a Java applet within a wiki page, a novel approach to implementing highly dynamic interactive environments within wiki frameworks.

Machine Learning String Tools for Operational and Network Security

Christopher S. Oehmen, Bobbie-Jo M. Webb-Robertson, Pat Nichols, Bill Nickless

◆ The goal of this project (MLSTONES) is to move toward proactive exploit detection by applying the mathematics and theory of bioinformatics. This approach is based on the concept that text strings describing biomolecules, such as genes and proteins are analogous to text strings that describe many aspects of the cyber universe. This project addresses the need 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 rule-based detection schemes is that we must first know what to look for, which is a challenge in the face of constantly evolving exploitive methodologies.

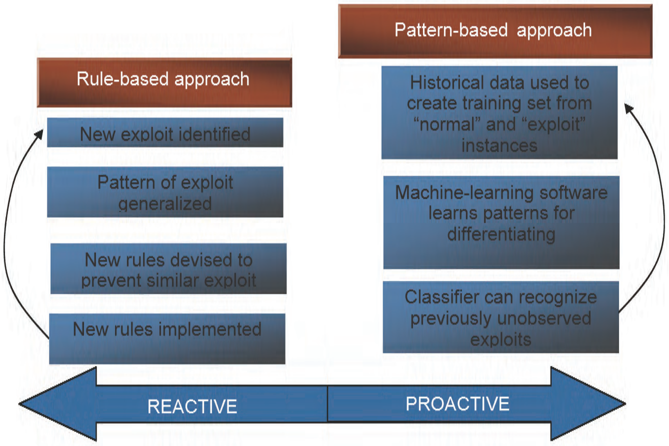
This project is directed at developing capabilities to enable the construction of a collection of solutions to challenges in cyber and network security. The primary approach is to train computational systems to recognize patterns of interest in string-based information (such as network transactions or legacy source code) by 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 will 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 the algorithmic and computational infrastructure needed to deploy this concept rapidly into new problem spaces of cyber security.

In FY 2008, this project accomplished the following:

Technical Analysis of Parallel Support Vector Machine Implementations. Finding efficient parallel support vector machine (SVM) implementations is a key to success of this project. Several SVM implementations were downloaded and built on a variety of architectures to profile their efficiency in terms of parallel scalability with respect to problem size, robustness, architecture utilization, and quality of resulting classifiers. Data sets of varying sizes were run on several platforms, including conventional clusters and shared memory machines to perform this testing. The results of this profiling effort have led to the design and prototype implementation of an efficient parallel SVM algorithm that will operate on large data sets.

Obtaining Network Transaction Data. In FY 2008, we received permission to use system log file datasets from PNNL and other sources for analysis in our work. The first sample datasets were delivered from the GRID computing center and from PNNL operations. These datasets detail system log messages that occur during normal and abnormal usage of networked systems. These datasets form the core of vectorization that will occur in FY 2009.

Algorithm Development. Support vector machine implementation developed under another LDRD project was originally designed for use in training classifiers for data-intensive applications (i.e., bioinformatics and cyber security). We focused our work on optimizing the training phase. To apply a classifier trained using this algorithm, one must classify new observations using the "support vectors" that result from SVM training. For data intensive application spaces such as cyber security, the classification itself becomes a large-scale calculation. This project focused on developing an efficiently-scaling SVM classification back-end to be used with the data intensive SVM training. The performance of this classifier was demonstrated for threaded and non-threaded implementations using as many as 1024 compute cores on a large-scale system, and shown to scale ideally to over 700 processors. This optimized classification process was used as an integral part of an entry into the Super-Computing 2008 conference visual analytics challenge competition won by PNNL. Efficient classification will be the basis of any domain-specific application of SVM, primarily a variety of applications in 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.

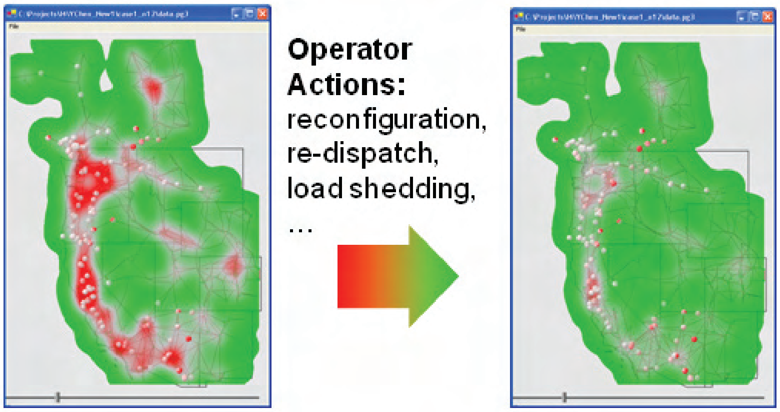
Managing Complexity of High-Volume Predictive and Adaptive Network Operations

Zhenyu Huang, Pak C. Wong, Kevin P. Schneider

◆ 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 decision support to network operators to ensure safe and reliable critical infrastructures. ◆

Critical infrastructures play an important role in modern societies. Their failures, such as power grid blackouts, would lead to the significant disruption of people's 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, complex data/information technology systems, and highly dynamic, nonlinear behaviors with numerous internal configurations and external factors. None of the complex network operations is fully automated; human-in-the-loop operations are critical. During an emergency, it is not uncommon for human operators to examine thousands of possible configurations in near real-time to choose the best option and operate the network effectively. In today's practice, network operations are largely based on experience with limited real-time decision support, resulting in inadequate management of complex predictions and the inability to anticipate, recognize, and respond to human errors, natural disasters, and cyber attacks.

A systematic approach is needed to manage the numerous predictions and choose the best option within the near-real-time constraints. This project aims to establish a decision support system to manage complex predictions and help operators predict potential network failures and adapt to adverse situations. The decision support system is a three-step process: predict imminent problems, predict consequences of problems, and predict effect of remedial actions. The resultant system will enable continuous monitoring of network performance, turn large amounts of data into actionable information, and maintain the integrity of the infrastructure.



Network risk-contoured map and remedial action evaluation.

In FY 2008, our efforts focused on the first two of the three-step prediction process. We successfully developed methods for network risk analysis and visualization, graph trending analysis, and configuration clustering. Some of the results were reported in an invited panel paper at the 2008 IEEE Power and Energy Society General Meeting.

Network risks are quantified as an index of individual network states with respect to their limits. Individual risk indices are then superimposed to form a network map to represent the collective risk of multiple possible configurations. Visual representation of risk indices is developed based on HaveGreen in C# using Managed DirectX and Gaussian color mapping with green/gray/red scale. The overall risk index of the network is calculated using a statistical analysis method that combines arithmetic and geometric average risk indices.

Based on the network risk analysis, trending analysis aims to observe and examine change in the risk index over time and predict whether the network is becoming more vulnerable, compromised, or more robust. The technical approach for trending analysis is a combined method analyses. Statistical analysis is used to calculate risk indices of individual regions, while structural uses a relation matrix to identify evolving patterns of network risk areas automatically. The resulting trend analysis has been proven to work for all complex evolving patterns in power grid examples.

A clustering analysis is performed to enable prediction of consequences of network failures. Clusters and patterns are identified and presented in association with the risk map, which will enable operators to focus on important information within the short time window in response to network emergencies. They can acquire necessary information interactively for specific geographical areas as well as individual configuration cases. Operators may study multiple configurations concurrently and compare scenarios.

Our FY 2009 effort will have two major focuses: further strengthen Step 1 by developing capabilities for multiple predictions and data integrity detection, and develop the Step 3 function for interactive evaluation of remedial actions. A prototype tool is expected to be developed at the end of FY 2009 to demonstrate the functionality of the decision support system.

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 and time-consuming process. By reducing the complexity of application construction, this project is designing software solutions that will make this application construction significantly easier and increase our capacity for scientific and threat discovery. ◆

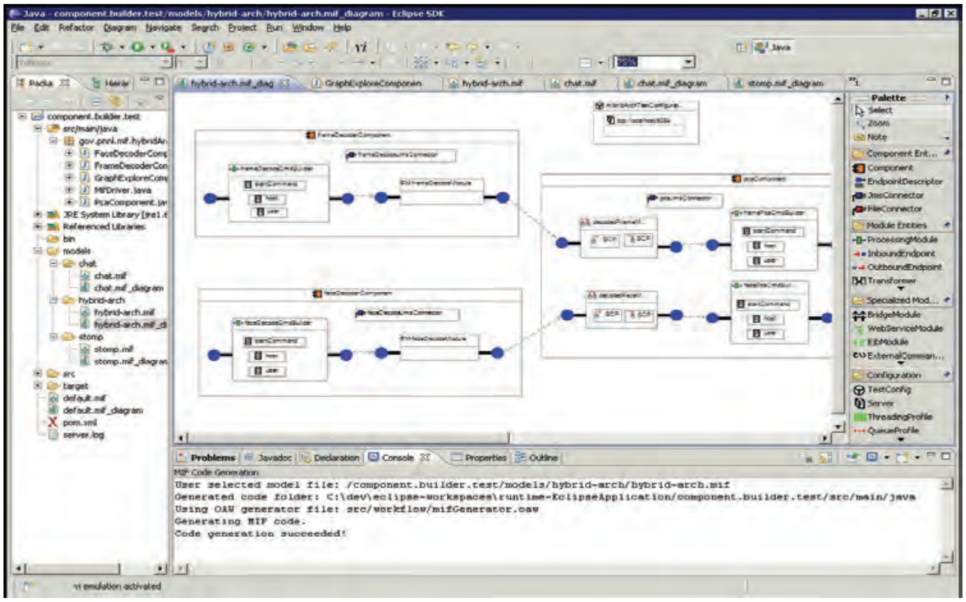
Advanced scientific simulations and analytical applications typically require the integration of multiple independently developed software modules into an integrated processing pipeline. This task is difficult because the software modules are not originally designed to interoperate. Consequently, application 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 this project, we have created the MeDICi integration framework (MIF) designed to make the integration of software modules into a pipeline easier. The MIF provides a consistent programming model and supporting software services that significantly lower the barriers to rapid interoperability and help automatically ensure 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 the MIF has the potential to have a broad, beneficial impact.

During FY 2008, we extended the core capabilities of the MIF platform created in FY 2007 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, the MIF Java code needed to execute the application is automatically generated. Three scientific papers have been presented at leading scientific and technical conferences, and our MeDICi wiki provides detailed documentation and programming guides for application developers.

We have validated the MIF platform and tools in several applications within PNNL. Currently, the MIF is being used as an underlying software technology in bioinformatics, 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 encouragingly, the MIF technology is able to provide significant value to the application designers involved in these projects. This provides considerable experience-based evidence that our approach is valid and that MIF technology is appropriate for use on the diversity of applications that we create at PNNL.

Our investigations have revealed several areas (i.e., pipeline run-time monitoring tools, support for catalogs of reusable components, increased platform scalability, and facilities for intelligent, adaptive behavior) where additional features and capabilities can be added to greatly increase the utility of the MIF. Each of these areas poses challenging research problems; therefore, we intend to pursue them during our final year of research for this project. The successful creation of these capabilities within the MIF platform will greatly enhance our ability to create, modify, and execute complex, integrated applications rapidly across all domains in science and intelligence analysis.



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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 Component Builder.

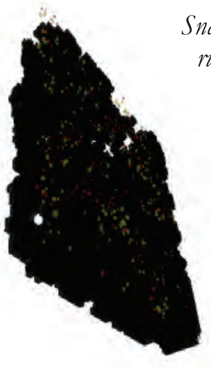
Modeling of Microbial Communities in Soil Aggregates

Lee Ann McCue, Haluk Resat

◆ Combating the rising levels of greenhouse gases in the atmosphere is essential for DOE's environmental impact mission. To accomplish this, we need to enhance our understanding of the microbial communities present in soil and rivers/oceans in order to develop a strategy for manipulation of those communities to enhance carbon sequestration in the soil and ocean. However, these ecosystems are extremely complicated, requiring 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. For example, soils are highly complex systems in terms of their composition, dynamics, and heterogeneity. It is estimated that 1 gram of soil contains ~10^9 bacteria and up to 1 km of fungal hyphae, and there is a vast diversity among the contained microbes. Modern sequencing technology has made it possible to map rapidly and accurately the content of an environmental sample, providing the species composition data needed for model development. In addition, the development of advanced simulation software enables the building of individual-based models of microbial ecosystems.

Modeling a complex and dynamic system such as a soil is a significant challenge but vital in order to enhance soil 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 to build three-dimensional agent-based community models. Computational techniques will be developed to analyze metagenome sequence data to infer microbial community composition, from which the community metabolic and functional capability will be inferred. The techniques and analysis of available soil aggregate data will be used to determine the variation in community structure and activity within and between soil aggregates.



Snapshot of a configuration representative of bacterial growth in confined soil geometries. It has been obtained in the simulations of a simple two-species composite system that uptakes ammonia and nitrous acid as the nitrogen-containing substrate in a geometry consisting of random pores. The size of the two species of the composite system is enlarged by a factor of 3 for clarity. The constraining spatial matrix is colored black, and the picture was obtained by rendering the configuration using the visualization program POV Ray.

We analyzed data from two types of DNA sequencing technologies to map the species in a microbial community. Both technologies targeted sequencing of the phylogenetically informative ribosomal RNA encoding genes; pyrosequencing with bar-coded primers was used for soil communities, and Sanger sequencing was used for river communities. The pyrosequencing service includes some quality control checking and data post-processing; thus, our activities focused on using statistical tests to identify significant shifts in the community composition (i.e., the species present and their abundance). The Sanger sequencing was provided as raw data, so we developed a set of Perl scripts to process the data for quality (eliminating poor quality sequence reads), combine sequence reads for complementary DNA strands, perform BLAST homology searches, and parse results to assign species identity to the sequences.

Building on recent advances in the modeling of bacterial ecosystems, we developed a basis 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 the dynamics of the cells to their internal kinetics in a single unified model; thus, our simulation platform makes it possible to use agent-based formalism without the requirement of a time-scale separation assumption.

As the time is propagated simultaneously, the cellular dynamics and cell decision-making rules can be made to depend on the internal state of the cells and on the state of their surrounding environment with better accuracy. Our simulation platform also allows for the use of kinetic models to describe the metabolic properties of the cells through mechanistic biochemical reaction network models. The cellular energy production/consumption and substrate utilization and product generation processes can be described at any desired level of detail in the kinetic models for the internal dynamics of the cells. Thus, one is not limited to treating the microbial ecosystems only in terms of energy and metabolite generation/consumption, and the user can define the energy and metabolite-related networks at the detail level that the goals of the study or the available data dictate. In addition, our platform is capable of including the three-dimensional taxis properties of the microbes in the models either at the level of individual cells or as a colony of any size. The simulation algorithms we are developing are being implemented in our *NWLang/NWKsim* software.

Modular Network Modeling of Inflammatory Pathways

Katrina M. Waters, Harish Shankaran, Brian D. Thrall

◆ This project will use particle-induced inflammation in macrophage and epithelial cells as a model system to compare standard gene regulatory to pathway-based modular networks. We will demonstrate new bioinformatic capabilities for mechanistic modeling of cell response pathways that describe paracrine interactions of multi-cellular systems from integrated microarray and proteomic data. ◆

A fundamental premise of systems biology is that the behavior of complex biological systems can be predicted through the integration of high-dimensional data and computational modeling. Developing mechanistic (predictive) models of cell signaling networks in mammalian systems is a challenge due to the inherent complexity of these systems, practical limitations in the data that can be collected at the systems level, and computational limitations for dealing with high-dimensional data. To address these challenges, we will develop modular network modeling approaches that capture the complexity of mammalian signaling networks and are computationally scalable and generalizable to new biological problems. This approach will combine computational methods for statistical ontology (functional) enrichment and network inference methods to reconstruct “cell response networks” from integrated genomic and proteomic data.

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, 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. Ultimately, the goal is to develop a strategy to create mechanistic models of cell response from integrated, high-throughput data using both experimental and computational approaches.

A primary objective in our first year was to determine an appropriate method for identification of functional modules from global response data (microarray/proteomics). Gene set enrichment (GSE) 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 GSE tool on our microarray datasets to determine how the macrophage response pathways change as a function of particle dose and time. Analysis of our dose-response experiment involving a 2-hour silica particle exposure highlighted how the processes changed from chemotaxis at low doses to defense response, followed by apoptosis processes at doses that were confirmed to cause cytotoxicity at 24 hours. These different cell processes represent either temporal shifts or new modes of action at higher doses. To test the hypothesis, we performed a similar analysis on the time course microarray data from macrophage cells exposed to silica particles for 1 to 24 hours.

Comparing the cellular process enrichment scores, we identified a cluster of processes associated with defense and inflammatory responses that appear to be temporally linked to apoptosis, which is dose-dependent. However, we also identified several clusters of cell processes that will potentially provide regulatory mechanisms for the dose-dependent transition from adaptive response to toxic response to build into our network model. In FY 2009, our bioinformatic efforts will migrate to the generation of gene regulatory networks and computational methods for isolating functional modules within network structures. We will compare these to our GSE modules to determine which functional units to build into our mechanistic models.

We also made substantial progress with the trans-well macrophage/epithelial cell co-culture system. We found that the macrophage cells grow well on the membrane surface of the top plate, but the epithelial cells do not. Therefore, we started our studies by treating the macrophage layer with silica particles and looking for changes in gene expression in the macrophage and epithelial cell layers. Using several gene markers, we were able to demonstrate an inflammatory response in macrophage cells after silica particle exposure but not a paracrine response in the epithelial cell layer despite the inclusion of interleukin 6, which is known to be an epithelial cell cytokine. However, when we analyzed the cell culture media for secreted proteins using an ELISA microarray system, we identified several proteins that exhibited synergistic regulation in the macrophage and epithelial cells through paracrine interactions.

In FY 2009, our co-culture experiments will focus on the reverse exposure system: treating the epithelial cells in the bottom chamber with silica particles and looking for inflammatory responses in both macrophage and epithelial cell layers. New experiments are underway to generate samples for microarray and proteomic analyses of epithelial cell response to particle exposure to identify marker genes and proteins for time- and dose-dependent expression studies. These data will be analyzed to provide the response networks for the other half of our paracrine system and start assembling our cell interaction network model.

Multiscale Computational Continuum Physics Solver

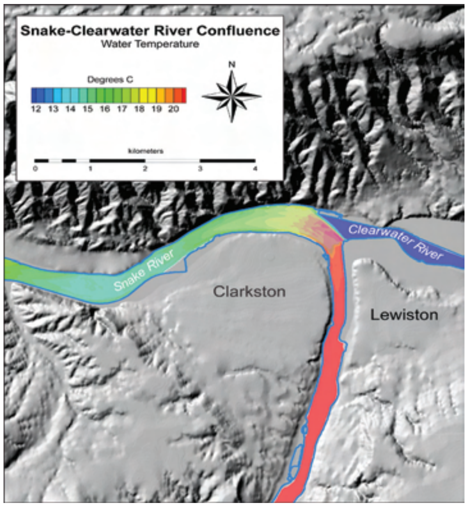
Marshall C. Richmond, William A. Perkins, Daniel R. Einstein, Andrew P. Kuprat

◆ We are developing the next generation of computational tools to predict the effect of environmental stressors on human and ecosystem health across scales ranging from nanometers to kilometers. ◆

A common need exists across the many science and engineering challenges facing DOE for verifiable physics-based modeling of complex systems over multiple scales. To address these needs, we are developing a high-performance computational continuum physics solver to simulate coupled fluid and solid mechanics processes in complex geometries with moving interfaces. The long-term aim of this effort is to create a flexible solver for research applications in biological, surface-water, and subsurface modeling that can span from microscales to macroscales. Our initial focus has been on computational fluid dynamics, heat, and mass transport applications.

We developed the base computational code Transient Environmental & Engineering Turbulent Hydrodynamics Simulator (TE2THYS), which is object-oriented and written in C++. The solver uses the finite-volume method that can be applied to linear and nonlinear partial differential equations. Equation systems solved using second-order time and space methods (e.g., total variation diminishing schemes). Linear solvers from the Portable, Extensible, Toolkit for Scientific Computation are also used. A key function is the ability to perform three-dimensional simulations using unstructured, multi-block, hybrid-cell computational meshes. This is important because it allows for the simulation of flow in complex geometries while resolving both fine- and coarse-scale processes by concentrating mesh resolution in regions of interest.

We validated the TE2THYS code for several benchmark laminar and turbulent flow cases. For laminar flow, the classic benchmark lid-driven cavity flow was selected. Validation results using a series of hexahedral meshes that are successively refined converged to the expected benchmark values as the mesh resolution was refined. Turbulent flow is simulated using Reynolds-averaged turbulence models. Specifically, the widely used k-E model with wall functions and the low-Reynolds number k-Ω models were implemented in TE2THYS and tested against direct numerical simulation (DNS) channel flow data. This comparison showed that the turbulence models functioned correctly and produced results in good agreement with the benchmark DNS data. Additional flow and transport cases such as laminar flow over a backstep, turbulent flow in a diffuser, and buoyancy-driven flow between heated/cooled plates were examined. These test cases showed that the code could simulate a wide range of complex flow conditions where density variations and flow reversals occur.



Te2THYS simulation of density-driven flow at the confluence of the Snake and Clearwater rivers. The simulation domain covers about 10 kilometers. Colder water in the Clearwater River is shown plunging beneath the warmer Snake River water.

In addition to validation cases, more complex flows were simulated. The code successfully computed the velocity distribution in physiological realistic bifurcation that is an idealized representation of the upper airway of a lung. A moving mesh of an impulsively started wave in a channel was simulated as a test of dynamic re-meshing in response to the computed flow field. The code successfully tracked the evolution of the water surface shape and internal velocity field.

Solving large problems using fine-scale spatial and temporal resolution requires a parallel version of the code that can be deployed on advanced distributed computing architectures. We used the PNNL-developed Global Array toolkit to create a parallel version of our code. The parallel version has been compiled and tested on a wide variety of computer systems. Parallel scaling tests were performed and showed good performance over a range of increasing processor numbers. We will continue work on improving the scaling performance and complete porting of the code to NERSC in follow-on work.

The new, parallel version of the code will be used to simulate problems in both subsurface and surface hydrology applications. An example of a surface water application is the mixing of water from rivers at different temperatures. The scale of this problem is on the order of several miles compared with idealized lung simulation on the scale of inches. In this application, denser, colder water plunges beneath warmer water in the confluence zone where the thermal gradients are thought to be important to migrating juvenile salmon. Simulations of water temperature and velocity distributions will be used in a follow-on project to help understand how fish respond to this complex physical environment.

Predictive Adaptive Classification Model for Analysis and Notification: Internal Threat (PACMAN-IT)

Frank L. Greitzer, Patrick R. Paulson, Thomas W. Edgar, Lars J. Kangas,
Lyndsey Franklin, Mariah Zabriskie

◆ This research aims to develop algorithms and methods within a predictive analysis and classification framework that address critical needs of federal agencies to detect and deter malicious insider activity. ◆

Espionage and sabotage involving computer networks are among the most pressing cyber security challenges that threaten government and private sector information infrastructures. Recent studies have identified a prominent role of psychosocial factors. This research has developed a framework for and implemented prototypes of core components of a predictive model-based system that takes account of psychosocial and cyber indicators of potential insider threats. 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 an initial limited test of the model using simulated data. We published one paper in a peer-reviewed journal and submitted another to a second. Additionally, our FY 2008 accomplishments are categorized below.

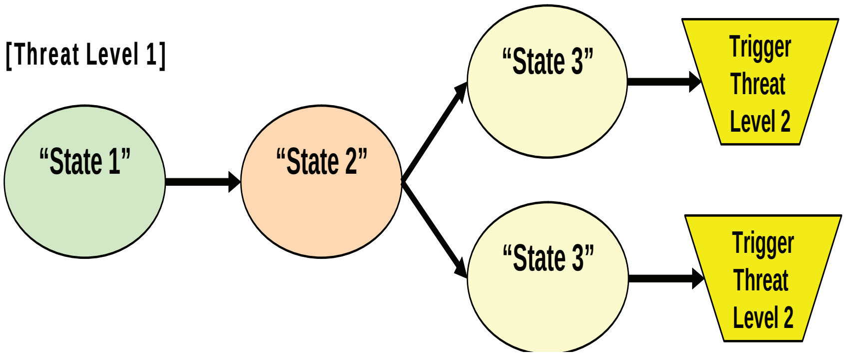
No single technique of intrusion detection or threat assessment gives a complete picture of the insider threat problem. Current practice in insider threat detection tends to be reactive, as it focuses on detecting malicious acts after they occur, with the aim of identifying and disciplining the perpetrator. In addition, there is no current system that integrates cyber and non-cyber (psychosocial) data into a predictive framework. Defining possible precursors in terms of behavioral, observable cyber indicators is one of the major challenges in developing a predictive methodology.

Predictive Modeling. At the foundation of our predictive modeling concept is a knowledge base of cyber and social indicators that informs all other components of the model updated or modified by outputs from these components. Model components perform the functions of data collection, data fusion, analysis, and decision-making. The analysis progresses from data to observations, indicators, and 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 where increased suspicion leads to more analysis, additional data collection, increased focus on some indicators, and additional attention to indicators that were not monitored previously (adaptation).

Implementation. A service-oriented architecture and object-oriented design provide an extensible, flexible, adaptive, and modular framework within which to implement the model. The main predictive component is the Reasoner, which uses Description Logic formulas to process observations of class membership and infer indicators. Behaviors are modeled as finite-state machines. The Reasoner assesses current indicators in combination with previously inferred indicators and behaviors to determine the likelihood of behaviors that represent a threat. Temporal relationships are expressed as finite automata; events move the automata from one state to another. In the illustrative figure, arrows represent transitions between states based on Description Logic rules. A dynamic Bayesian network stores the current position or status in the finite state machine.

Additional accomplishments include the development of an initial user interface that demonstrates 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.

Our FY 2009 research will focus on refining the model, extending its generality with a broader set of threat scenarios, and conducting a formal evaluation study.



This model demonstrates that both cyber and psychosocial data may be integrated into this predictive classification and decision framework.

Scientific Metadata Services (SMS) Architecture

Eric G. Stephan, Abbie L. Corrigan, Chandrika Sivaramakrishnan

◆ To protect the investment of vast amounts of raw scientific evidence, we need to provide software services capable of making the data more accessible. Accessibility is made by identifying software services that help users analyze their data through the use of provenance, metadata, and 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 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. 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 one day 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.

The foundation of this research is to identify common software services that will be used for the analysis of high-performance computational and experimental data. The SMS will be designed to scale through the 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.

In FY 2008, our research encompassed studying scientific data, usage patterns, and data sources that tie 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 the entire users' present needs, give a dynamic perspective of the users' ever-changing needs, and adequately identify communities of users having similar needs.

Our first step was to determine how to extract scientific metadata. We chose harvesting because we wanted to find an unobtrusive way to collect metadata without changing the culture of scientists saving and accessing data files. To test this method's effectiveness, we deployed a generic harvester to extract knowledge from over 15,000 nuclear magnetic resonance experiments that were coupled with numerous quantum chemistry simulated predictions using a high-performance computing computational chemistry code, NWChem. Because the extracted knowledge was graph-like in nature, we relied on a resource descriptive framework database to collect the harvested results.

Our initial findings showed that the experimentalists found it valuable to be able to search their archived data rapidly and could envision having customized views of their data to support various downstream users; thus, any future tool must emphasize both view development and scalability. With a solution to extract metadata in hand, a question appears about how to detect usage patterns in archived scientific data and the methods of characterizing these usage patterns as requirements for specifying services. To detect usage patterns, we archived scientific data files and knowledge about the users by mining existing administrative paper citations and the data repositories themselves. We categorized the mined data sources five categories: citations, archive metadata, data formats, administrative reports, and relating user proposals. From these sources, we determined domain focus, user location, institution affiliation, social networks, archival behavior, and growth trends. From the results, we learned that a growing number of remote users accessing PNNL resources rely on terascale resources. We also found the need for specialized search engines because we have hundreds of terabytes of data that exist in archived files.

Our preliminary research showed that it is possible to establish living requirements by building knowledge repository from identified store, mining requirements collection points to verify problems and solutions, identify new services and assess their impacts, and identify overlaps and interdependencies between domains. While these results did not yield specific analytical requirements, we are confident through our data harvesting and mining methodology that we will gain insights by fine-tuning the approaches toward specific scientific aims and goals within datasets.

In FY 2009, our goal is to participate actively with the eXtremely Large-scale DataBase pilot program, which is at the forefront of developing scientific databases for complex science. We will seek to engage in activities that identify analytical tools for targeted scientific communities relevant to the DOE mission and develop a proof-of-concept showing its benefit to specific researchers within those communities.

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 (TDMAA) addresses the critical needs of national security for resilient, self-defending networks to decrease the time between attack onset and remediation. ◆

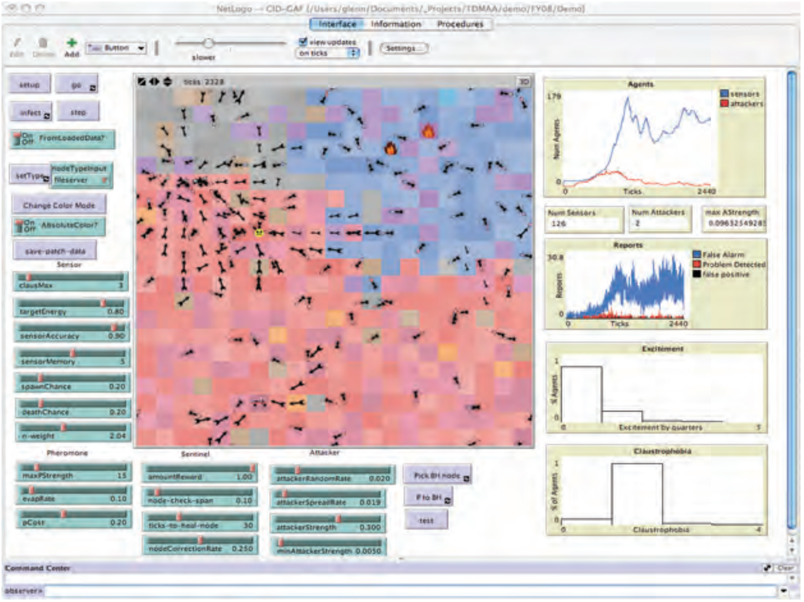
The tremendous speed of attackers on today's networks and machines has driven defenders to rely on automation to separate misuse attempts from the legitimate use of cyber resources. The ultimate cyber defense objective for many is a completely autonomous system that defends computer resources in the background, allowing normal business to proceed unobstructed. Humans will always be responsible for the actions of their machines; thus, 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.

Tactical deployment and management of adaptive agents provide a framework for cooperative cyber defense for groups of interdependent enclaves 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 generally do not share policies. Examples include the computers and networks supporting our national electric power grid; distributed, heterogeneous computing collaboratories used in open science; or computer equipment used to support partner countries in coalition warfare. We seek to discover ways that humans can exert supervisory influence while retaining rapid, adaptive system 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.

In FY 2008, we more carefully defined the entire framework and each relationship contained within. We analyzed system failure modes and inherent weaknesses in our algorithms in an effort to understand the ideal conditions and constraints for using this approach to cyber security and devised an initial approach for trust management to mitigate these 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 in FY 2007, leading us to create an algorithm to translate the discontinuous geography of cyber space. A screenshot of the revamped simulation is shown in the figure. Finally, we have done preliminary automated analysis work using support vector machines to predict/detect failures at nodes. We took syslog data from PNNL's 1100-node MPP2 cluster computer and used it to detect disk failures with 80% accuracy within a 48-hour window. This approach can use the same technique's train classifiers to predict or detect events of cyber security interest.

This project will continue into FY 2009 with the following tasks: 1) field a prototype CID system on a cluster or grid computer and study its aptitude for discovering and resolving specific types of cyber attack, 2) define the hierarchy of agents and their interactions with humans, 3) incorporate trust management into the agent hierarchy, 4) publish papers to capture the bulk of this work done over its three-year life span, and 5) engage clients that would benefit from our research so that the work may continue as a funded project in out years. Accomplishment of these goals is critical to the success of this project and research equipped with tools to match the growing threat from network-based attacks.



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TDMAA simulation model using ant-colony algorithms and multiple data sources.

Nuclear Science and Engineering

Adaptation of Existing Probabilistic Risk Assessments to Support Reactor Aging Management

Stephen D. Unwin, Stephen R. Gosselin

◆ This project is intended to help ensure that regulatory decision-making on reactor life extension is properly risk-informed such that reactor aging management 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 risk-effective test, maintenance, and surveillance strategies for reactor aging management. ◆

Probabilistic risk assessment methodology has provided the principal basis for risk-informed decision-making in the nuclear power industry, yet limitations on conventional probabilistic risk assessment methods constrain their value as effective tools to address the aging effects on facilities and quantify risk and reliability impacts of component aging management strategies.

This project, which began in early August, is aimed at establishing 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 in this expansion of methods is to model age-dependent equipment failure rates and include in the probabilistic risk assessment model certain classes of components (principally passive) that have not been captured traditionally in probabilistic risk assessment studies. This is critical since it is passive components generally not amenable to refurbishment or replacement that are expected to govern the accident and operational risks associated with an aging fleet of nuclear power plants.

Probabilistic risk assessment and safety and value decision technologies will provide the framework in which the significance of materials reliability issues can be assessed and important areas for improvement in structural materials reliability and aging management can be identified. Although probabilistic risk assessment 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 of our work is to establish the methodological basis for adapting existing probabilistic risk and reliability studies to support integrated reactor aging management programs for passive nuclear power plant components. We will develop, document, and apply a methodology to a limited-scope probabilistic risk assessment model and in subsequent years to larger-scale models. Software will be created that interfaces with existing probabilistic risk assessments to support third-party application of the methods. Expected outcomes include a documented methodology for augmenting an existing probabilistic risk assessment model to allow the risk impact of aging passive components to be determined, alternative aging-management strategies to be evaluated, and a demonstration application of the methods based on a limited-scope probabilistic risk assessment model.

A brief preliminary activity was identified for FY 2008 to obtain probabilistic risk assessment models and associated plant documentation that could be used as the basis to initiate methods development. Communication with Nuclear Regulatory Commission (NRC) staff led to the conclusion that homeland security constraints would impede the acquisition of a probabilistic risk assessment model from NRC; therefore, we resorted to a different approach. Based on printed fault trees in NRC reports – principally, NUREG-1150 – we were able to reconstruct a limited set of models using the SAPHIRE probabilistic risk assessment software. Specifically, the Surry Plant Auxiliary Feedwater System and High-Pressure Injection System models were chosen for reconstruction. The Surry assessment has been tentatively selected for analysis to take advantage of the project team's plant knowledge from previous projects. This partial probabilistic risk assessment model of the Surry Plant will be appropriate for initial methods development. We also identified and obtained relevant plant system engineering drawings and isometrics from the NUREG/CR-6923 document and other sources to facilitate interpretation of the reconstructed probabilistic risk assessment models.

An extensive literature review was conducted as part of the preliminary effort. 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 literature review, which will continue throughout FY 2009. In addition, initial FY 2009 activities will include developing a screening methodology to determine which components and modes of aging degradation should be incorporated into a probabilistic risk assessment model such that it can provide a robust technical basis to for reactor aging management. This methodology will be tested through application to the probabilistic risk assessment models developed in FY 2008. It is anticipated that the same probabilistic risk assessment models will also provide a baseline resource in the subsequent development of a methodology for the probabilistic quantification of the component failure events selected for inclusion.

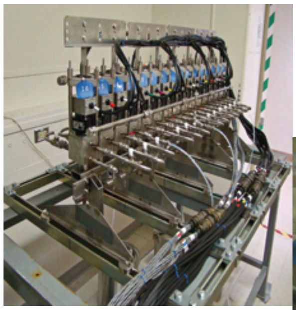
Counter-Current Solvent Extraction Behavior of Neptunium

Brady D. Hanson, Samuel A. Bryan, Tatiana G. Levitskaia, Justin M. Billing, Amanda M. Johnsen

◆ A transuranic element produced in nuclear reactors, neptunium is important to high-level waste disposal because of its long half-life. As such, its behavior in the nuclear fuel cycle is imperative to understand within the context of the global expansion of nuclear energy. ◆

The recycling of transuranic elements from nuclear reactors is a significant means to minimize long-term environmental impact from high-level radioactive waste disposal in geologic repositories (e.g., Yucca Mountain). The chemical processes used to separate various constituents from irradiated nuclear fuel originated in World War II as part of the Manhattan Project. Since then, various methods have been developed and industrially deployed to process irradiated nuclear fuel for civilian and defense purposes. This project was initiated to study neptunium (Np) chemistry in the context of transuranic recycle from irradiated nuclear fuel. Management of Np is of critical importance in developing and implementing a closed nuclear fuel cycle, a concept that has gained renewed interest in the United States. The behavior of Np in dynamic solvent extraction systems is difficult to predict because the oxidation state of this transuranic element is sensitive to the solution conditions. Counter-current solvent extraction experiments will provide significant insights into the Np chemistry under plant-prototypic process conditions that cannot be obtained from batch contact experiments necessarily conducted in a non-prototypic co-current manner. In addition, this project will develop online spectroscopic process monitoring capabilities to enhance process control and diagnosis.

We constructed a solvent extraction test installation to serve as a platform for investigating neptunium redox and coordination chemistry using online spectroscopic process monitoring techniques under plant-prototypic counter-current solvent extraction conditions. Prior to the solvent extraction separation technique, the irradiated fuel is dissolved in nitric acid. The aqueous solution is mixed with an immiscible solvent chemically designed to extract desired constituents preferentially from the nitric acid solution. In an industrial configuration, the aqueous and organic solutions flow in opposite directions (counter-currently) to maximize the extraction efficiency. Industrial processing of irradiated nuclear fuel has focused mainly on uranium and plutonium extraction using the solvent extraction process PUREX. Within the current context of nuclear energy expansion, there is a need to investigate neptunium behavior in the PUREX process.



Centrifugal contactor apparatus first as a mock-up and then as installed in the shielded glovebox.

Initially, prototypic counter-current experiments were performed using small-scale versions of the process e equipment (centrifugal contactors) expected for industrial deployment in conjunction with online spectroscopic process monitoring equipment. This integrated experimental system enables us to conduct experiments rapidly, obtain new insights into neptunium liquid-liquid distribution behavior, and optimize neptunium extraction. Initial experiments were performed based on process conditions similar to that encountered in traditional fuel recycling flowsheets. Later studies will investigate co-extraction and the recovery of neptunium with plutonium to improve the proliferation resistance of the processing flowsheets.

Non-radiological shakedown and hydraulic testing of solvent extraction contactors were completed in FY 2007. Work in FY 2008 has focused on the design and installation of the solvent extraction testing apparatus in a radiological glovebox. Sixteen 2-cm centrifugal contactors were assembled and tested as a mock-up prior to being installed in a 1.3-cm lead shielding glovebox. Ancillary equipment installed in the glovebox included stainless steel tanks for feed, scrub, solvent, and product solutions as well as balances to track the mass of material transferred into and out of these tanks. Process control software was developed using the LabView data acquisition and control software package that allows complete remote operation, control, and monitoring of the process equipment. A flow cell for adapting the Raman and ultraviolet-vis probes to the inter-stage lines of the contactor apparatus was designed, fabricated, and tested with water. Preliminary testing indicates that the flow cell design is compatible with the spectroscopy techniques; further testing with process solutions will proceed in preparation for installing online monitoring within the glovebox.

Online monitoring activities completed during FYs 2007 and 2008 included quantitative demonstration of spectroscopic neptunium detection in a simulated dissolved irradiated nuclear fuel matrix using ultraviolet-vis near-infrared spectroscopy. Test solutions containing simulated dissolved irradiated nuclear fuel and loaded PUREX solvent were measured using Raman spectroscopy. These measurements confirm that nitric acid and uranyl nitrate can be monitored in real time. FY 2009 testing will investigate neptunium behavior using online spectroscopic techniques in real time using flow cells connected to the centrifugal contactors.

Develop an Expert Elicitation Process for Use in Evaluation of Proliferation Resistance of Nuclear Energy Systems

Michael D. Zentner, Garill A. Coles, Timothy E. Seiple

◆ As the use of nuclear energy spreads, the proliferation resistance of new energy systems will need to be evaluated. All international compacts such as the Generation IV International Forum, the Global Nuclear Energy Partnership (GNEP), and the International Project on Innovative Nuclear Reactors and Fuel Cycles include minimizing the potential for nuclear proliferation from nuclear energy systems as an important goal. ◆

Within the U.S. government interagency community, a growing need exists to perform timely evaluations of the proliferation resistance of nuclear energy-related processes and/or facilities. Currently, to support a typical request for timely information about the proliferation resistance of a process and/or facility related to nuclear energy at the national, regional, or international level, subject matter experts are tasked to perform an assessment that normally takes between a few weeks to months to complete. Such work is typically done in an informal and unstructured fashion, and the evaluation may not always be repeatable or supportable if followed up by more detailed technical evaluation. This project will develop a consistent and systematic technology-based method for performing a timely analysis based on an expert elicitation process for evaluating proliferation resistance consistent with and building upon the detailed analytical methodology being developed by the Generation IV International Forum Proliferation Resistance and Physical Protection Working Group. The analysis process will be based on a set of structured, thoroughly documented procedures designed for increasingly detailed levels of effort. The results of the analysis will identify the proliferation resistance of “process/facility x.” Procedures will be written for several levels of detail depending on the purpose of the assessment, the time available to perform the work, and the level of detail required. Our approach will ensure the quality, comprehensibility, and credibility of the results.

In FY 2007, a structured approach for expert elicitation-informed proliferation resistance assessment was developed. Our approach prescribed a process for evaluating the proliferation resistance of a nuclear energy system using subject matter experts who are familiar with a nuclear facility type, nuclear system process, international safeguards, and other key inputs. Using the procedure, subject matter experts are guided through an elicitation process to determine the plausibility of abrogation, concealed diversion, undeclared production, or potential misuse of declared facilities based on either a given or a developed threat characterization of a particular process or facility. Factors considered include materials processed or used, facility type and configuration, process used, and quantities present. The process consists of identification and definition of the problem to be assessed, selection and training of experts to perform such an assessment, threat and system analysis, and characterization of proliferation resistance. We prepared an original draft procedure and used it to assess the proliferation resistance to material diversion of an example nuclear energy system. A draft report was written and, using lessons learned from this task, the procedure was modified. A new version was under preparation to be tested.

In FY 2008, the new version of the procedure was completed. One of the lessons learned during the testing was that documenting the many elements of the process was a time-consuming, complex task. A prototype computer tool was prepared and tested that provided a structured approach for guiding and recording the elicitations. After testing, the prototype tool was used in a set of actual studies for the GNEP Grid Appropriate Reactor Proliferation Resistance Program. In this set of studies, a multi-lab team of proliferation resistance, safeguards, and operational design experts evaluated and compared the proliferation resistance of three reactors. Three pathways were examined for each facility, and the results were compared. After initial meetings, a series of video conference were conducted using the prototype tool, which provided a means for the assessments to be performed without the requirement for all teams to travel to a central location.

Based on lessons learned by using the prototype tool, a more sophisticated tool was created based on a database approach rather than the Excel spreadsheet methodology. This final tool was used in a set of four studies for the Generation IV International IV Proliferation Risk Reduction Program (PRR-3). Again after initial meetings, the use of the tool allowed a series of video conferences to be performed, completing that phase of the PRR task. A final development was the use of the PC-based Microsoft Live Meeting technology, which allowed participants to use their own computers and participate in the elicitation on an individual basis rather than gathering in the video conference room. This provided a more convenient approach for performing the elicitations. It is expected that the methodology and computer tool will be used in follow-on studies in FY 2009.

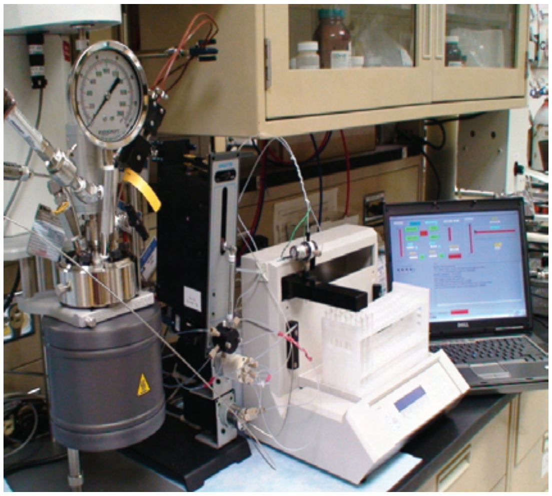
Dissolution of Actinides Under Oxidizing Conditions for Nuclear Energy Applications

Shane M. Peper

◆ 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 of paramount importance that efficient, preferably environmentally benign ("green") processes be available to reprocess current and future inventories of commercial spent nuclear fuel (SNF). ◆

To date, the Plutonium Uranium Redox EXtraction (PUREX) process is the only technology globally employed at a significant scale to reprocess SNF. This liquid-liquid extraction process uses highly concentrated HNO_3 solutions (6-11 M) at elevated temperatures as the head-end process for dissolving SNF. 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 has several short-comings based on design, such as 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 from SNF by leaching it from the irradiated fuel using optimized process conditions. Removing uranium from spent fuel will dramatically reduce the amount of radioactive waste requiring long-term storage, since U comprises ~94% of the total SNF generated by commercial power reactors in the United States.

The work being done in 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 in order to design a green process for SNF dissolution. 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 SNF reprocessing. It is anticipated that this technology will be integrated into existing reprocessing flow sheets, such as UREX-1a or as the basis for developing an entirely green alkaline SNF recycling process.



Photograph illustrating the automated digestion system developed for rapidly performing U(IV) oxide dissolutions.

This year, research focused in four areas: initial UO_2 dissolution studies, synthetic fuel fabrication, design and fabrication of an automated system for monitoring actinide oxide dissolutions, and solid-state chemistry. For initial UO_2 dissolution studies, we examined the effect of several key experimental parameters on the rate of U dissolution, including peroxide concentration. Synthetic fuel pellets containing a mixture of ^{233}U and natural uranium were fabricated for future dissolution studies using the "closed" digestion vessel described in the subsequent research area. This fabricated fuel has a much higher specific activity than pellets made exclusively from natural U and was chosen so that scintillation counting could readily be used to monitor U oxide dissolutions.

Significant work was done to design and fabricate an automated system for dissolution experiments. This system accommodates aqueous or gaseous reactant feeds and allows for microliter volumes of dissolver solution to be extracted and collected for on- or off-line analysis. Current efforts explore the chemistry of cerium, which has been shown to exhibit chemical tendencies analogous to plutonium.

For FY 2009, research will focus on testing the automated dissolution system using radioactive materials and examining several key dissolution parameters, including carbonate concentration and countercation, stir rate, and the use of gaseous reactants. Additionally, we will study the dissolution of other U oxides such as U_3O_8 and UO_3, both relevant to different parts of the nuclear fuel cycle. The dissolution of transuranium oxides, including NpO_2 and PuO_2, will also be studied. Solid-state chemistry studies will be pursued for U, Np, and Pu in addition to the behavior of these elements in oxidizing alkaline solutions containing peroxide. Once we have optimized the dissolution parameters and determined the key solution and solid-state species that will predominate, we will test our approach on irradiated spent nuclear fuel and work toward developing a new process flow sheet.

Electrochemical Separations for Enhanced Safeguards Analysis

Douglas C. Duckworth, Matt Douglas, Scott A. Lehn, Martin Liezers, Shane M. Peper, Jon M. Schwantes

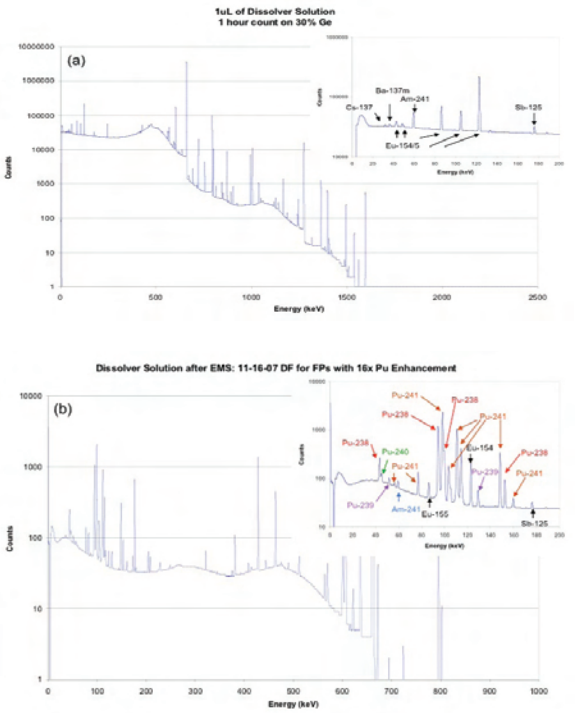
◆ This project supports the safeguards community by providing improved methods for accurate and timely measurement of accountable material mass at fuel reprocessing plants, thereby improving materials control and accountability. ◆

Safeguards accountancy at a nuclear fuel reprocessing facility depends on an accurate and timely measurement of accountable material mass (e.g., plutonium) in both the head-end fuel dissolution tanks and various process streams within the remainder of the plant. Current methods are based on destructive analysis of extracted samples that can take days to complete and months to verify. An online method is needed to measure the mass of accountable materials in process streams directly. Experiments are being conducted to extend novel multistage recognition technologies in an aqueous-based (nitric acid) separation technique that uses both redox and complexation chemistry together to isolate uranium (U) or plutonium (Pu) selectively from complex matrices. Essentially, accumulation of U or Pu is turned off and on with an applied dc potential. Distinctly different from pyroprocessing and traditional liquid and column extractions, only a potential step is required to accumulate and isolate components for analysis.

Project goals are to conduct studies to: 1) scale up sampling technology to process representative sample sizes, 2) demonstrate operation in complex chemical matrices and environments, 3) simulate gamma spectroscopy measurements post-isolation, and 4) develop and test bench-scale nondestructive and destructive analyses sampling applications for safeguards. These studies will demonstrate the technology's applicability and utility for safeguards monitoring. Successful completion of this project will result in a demonstrated technology to simplify and extend online nondestructive analysis capabilities by isolation of targeted components prior to nondestructive analysis. In addition, it will provide a safe and rapid means of sampling for destructive analysis.

We will test the "switchable" separations to isolate actinides or fission products from reprocessing streams for rapid, nondestructive, and interference-free analysis (neutron, gamma spectroscopy) of accountable materials. The separation relies solely on the potentials applied to modified target electrodes, so it is critical to understand the response of multiple elements in a complex mixture. During FY 2008, electrochemical cells were designed and fabricated to increase surface area for enhanced capacity. Matrix studies were performed to measure selectivity and matrix reduction factors. Measured by inductively coupled plasma mass spectrometry, these reduction factors were used to perform simulations of gamma spectroscopy for Pu in a typical dissolver solution.

The ability to isolate and concentrate plutonium selectively on a surface via potential control and rinse-interfering radioisotopes back into the process stream was demonstrated. This result should allow otherwise impossible spectroscopic measurement of Pu to be used. Using the experimentally determined EMS reduction factors for a simulated dissolver solution, gamma spectroscopy was simulated using SYNTH. The gamma spectrum for a dissolver solution containing the relative multi-element concentrations of 1 metric ton of PWR fuel assembly (50 MWd/kg burn-up and 10 years of cooling) was calculated. The results are shown in the figure both before and after EMS. As a result of EMS, the continuum background is reduced by a factor of 1000 which, in combination with Pu concentration effects on the electrode surface, allows Pu isotopes to be measure above background according to this simulation. It is envisioned that an isotopic spike would be added during dilution of the process stream solution for quantification in FY 2009.



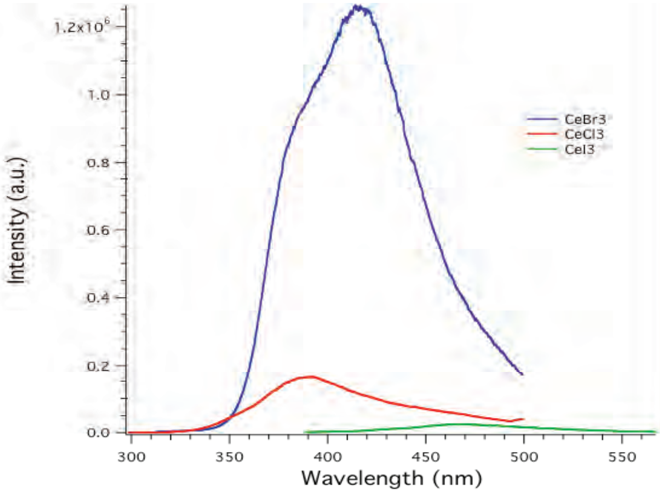
SYNTH-generated gamma spectra of dissolved spent fuel a) before and (b) after EMS separation based on experimentally derived reduction factors. Notable reduction occurs in the background, and Pu isotopes are significantly present above background. Gamma-spectroscopy and EMS-based destructive analysis using true dissolver solutions are planned in FY 2009.

Guided Discovery Demonstration Project

Gordon L. Graff, Daniel W. Matson, Bret D. Cannon, Kim F. Ferris, Jonathan L. Male, Brian D. Milbrath, Larry C. Olsen

◆ An urgent need exists for development of better scintillators for use in national security applications, yet the discovery of materials with significantly improved performance is rare largely due to the lengthy process used to screen samples. For the first time, a proof-of-concept demonstration showing the advantages of using a science-based approach to discovering improved radiation detection materials was completed. Predictions from materials informatics were coupled with high-throughput combinatorial screening techniques to map an entire family of rare earth halide scintillators. ◆

The development of new compositions suitable for use as scintillator materials has been limited by either the cost and time involved in the growth of sufficiently large (1 cm^3) single crystals of the proposed materials based on theoretical predictions or by the use of combinatorial approaches based on powder synthesis methods. While amenable to the rapid synthesis of a wide variety of compositions, the measured response of powder samples is often inaccurate since the properties are dominated by surface effects, small crystallite sizes, and high defect concentrations as a result of the powder preparation methods. The primary objective of this work was to demonstrate that important scintillator performance properties (such as brightness and optimal dopant concentrations) could be measured using thin film samples with greater accuracy than powders and ultimately minimize the number of new "compositions-of-interest" requiring time-consuming single crystal growth. A second objective was to validate PNNL's new materials discovery approach that combines theoretical predictions with high-throughput synthesis/screening techniques to map entire composition regimes rapidly.



Photoluminescence measured on thin-film samples deposited using combinatorial deposition methods. Light yield trends in thin film samples are consistent with crystal data.

Recent efforts to screen a wide variety of potential scintillator and luminescent compositions through the use of combinatorial thin film synthesis methods have been encouraging. Thin film samples prepared using simple thermal evaporation of CaF_2/EuF_2 powder mixtures was accomplished and characterized for photoluminescence and alpha particle response. Measurements performed on CaF_2:Eu films (10 µm) at Eu activator concentrations of 0.1%, 0.2%, and 1% showed maximum light yield at 0.2% dopant levels; consistent with commercial crystals. Thus, dopant optimization could be determined in a few days rather than the months required for crystal growth.

Efforts then focused on deposition of continuous compositional gradients in the $CeCl_3$:$CeBr_3$ and then the $CeBr_3$:CeI_3 systems using two spatially separated evaporation sources in a 1 m^3 vacuum chamber. The entire range of compositions across the binary was deposited in one machine run across a single substrate holder. Once calibrated, sufficient samples could be prepared and analyzed within one week (triplicates or quadruplicates) to provide statistically relevant data.

Elemental analysis using energy-dispersive spectrometry-confirmed uniform substitution of the anion (Cl to Br to I) across the entire compositional range with an accuracy of approximately ±10 atom %. X-ray diffraction analysis revealed uniform, predictable expansion of the crystal lattice upon substitution of the larger Br anion into the $CeCl_3$ lattice with no change in the hexagonal crystal structure. Photo-luminescence measurements were also used to determine the brightness, timing, and emission spectra of the varying compositions. A general shift in the emission peak maximum was observed consistent with the lattice expansion of the matrix and the measured lifetimes (~14-17 ns) consistent with reported radioluminescence decay times of ~17 ns. The light yield also increased steadily with increased Br substitution.

Several interesting findings surfaced when mapping the $CeBr_3$ to CeI_3 compositional range. Though energy-dispersive spectrometry analysis confirmed that the elemental composition was changing in a uniform manner, X-ray diffraction analysis revealed a change in crystallographic structure from hexagonal to orthorhombic upon increasing substitution of I anions into the $CeBr_3$. The brightness dropped dramatically over a similar compositional range. The $CeCl_3$ emission spectra maximum was further red-shifted and had approximately 1/50th the intensity of $CeBr_3$. Further, the photo-excited state of $CeCl_3$ yields a two-component decay with an extremely fast (300 ps) major component, which indicates that non-radiative pathways dominate the photo-physics of CeI_3.

Development of several specialized encapsulation and handling techniques were required to prevent hydrolysis during deposition, sample transfer, and analysis of the extremely hygroscopic rare earth halides. Even minute levels of hydration/hydrolysis dramatically affect the measured film performance and lead to inconsistent results. The significant increase in surface area coupled with this extreme hygroscopicity would make similar analyses using powder samples nearly impossible. For this one-year project, sample characterization was limited to thickness, composition, structure, and photoluminescence properties to demonstrate the validity of the approach. Additional property screens such as melting point, hygroscopicity, bandgap, or others could be added for additional refinement.

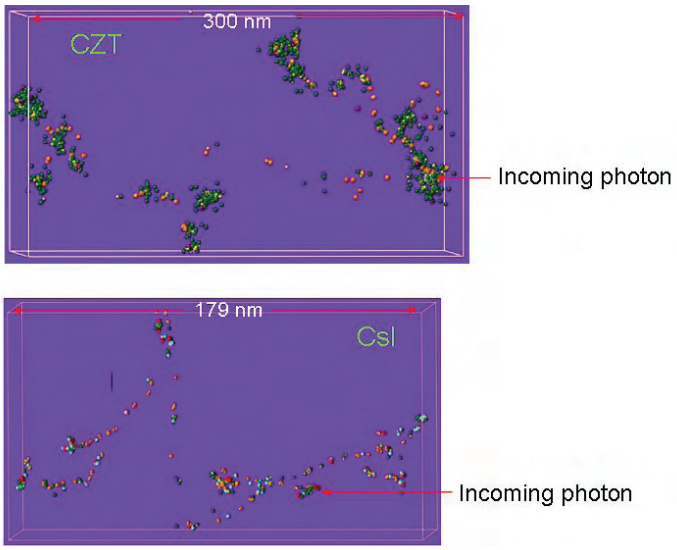
Though significant follow-on work remains, a viable new approach for rapidly identifying and validating new classes of scintillating materials has been demonstrated. By combining the computational/predictive power of directed materials informatics with high throughput combinatorial synthesis approaches, a new paradigm in radiation materials discovery can emerge. This approach does not eliminate the need for final crystal growth and full characterization of the materials' response to ionizing radiation. Rather, the methods identified here enable mapping of much larger compositional ranges, identifying compositional regions of highest interest, and minimizing the number of compositions requiring full crystal growth.

Modeling of Energy Transfer and Associated Variance in Gamma Ray Detector Materials

Fei Gao, Ram Devanathan, Yulong Xie, Renee M. Van Ginhoven

◆ This project provides insights into the fundamental quantum mechanical mechanisms that control energy transfer and loss of the fast electrons created by gamma rays to understand signal variance in both scintillators and semiconductors using computer simulation. Together with ab initio calculations, an advanced Monte Carlo method was developed to study information carrier production that accurately describes the intrinsic variance, the mean energy required to create, and the spatial distribution of electron-hole pairs. ◆

The development of new, improved materials for radiation detection is driven by national security and fundamental science interests to understand materials performance. An effective scientific approach requires gaining a fundamental knowledge and understanding of the interaction of fast electrons created by gamma rays with materials as a means to accelerate radiation-detector materials discovery and development. The interaction of gamma rays with matter results in the generation of fast electrons that lose energy mainly through indirect (bremsstrahlung) and direct (phonons, plasmons, electronic excitations) energy transfer. The primary requirement for radiation-detector materials is to detect and resolve efficiently the energy spectrum of information carriers. A Monte Carlo method to provide solutions of the quantum mechanical description of excited energy transport is well suited to this problem.



Comparison of nanoscale spatial distribution of electron-hole pairs between CZT and CsI.

During FY 2005, the first version of a new in-house Monte Carlo code to simulate the interaction of gamma rays with semiconductors and subsequent energy partitioning of fast electrons was developed. In FY 2006, the code was extended to simulate the interaction of gamma rays in gaseous scintillators such as gaseous xenon (Xe) and used to investigate various quantum mechanical processes for energy loss of photons and fast electrons over the energy range from 50 eV to 2 MeV in Si and germanium (Ge). For FY 2007, the code was further extended to simulate the energy partitioning of fast electrons for a more complex scintillator (CsI) and compound semiconductor (CdZnTe). The mean energy required to create an electron-hole pair (*W*) and Fano factor (*F*) were evaluated for several semiconductors. By fitting the data, a new relationship between the average energy for electron-hole pair production and band gap was established. A significant achievement of this project was the development of a new capability that deals with spatial distribution of electron-hole pairs in semiconductors and scintillators.

During FY 2008, a multiple-scattering theory was adapted into the Monte Carlo code, and it can be now used to study the spatial distribution of electron-hole pairs in materials at both low and high energies (up to a few MeV). The code has been further benchmarked in scintillators (CsI and $LaBr_3$) in terms of energy resolution, *W* values, and spatial distribution of electron-hole pairs. The contribution of individual excitation processes to the signal variance has been investigated in detail, and the dominant processes have been determined. These results clarify if non-linearity is associated with the intrinsic properties of these materials or due to long-time evolution of electron-hole pairs with microstructures. Further, the code has been developed to include the final energy distribution at the different sites of electrons created.

The figure shows a comparison of the nanoscale spatial distributions of electron-hole pairs between CdZnTe (CZT) (a) and CsI (b). The results clearly demonstrate that the distribution of e-h pairs is clustered in CZT, while in CsI, it is along tracks. The density of electron-hole pairs in the clusters is high in CZT, while it is low in CsI. In addition, the number of e-h pairs in CZT is much larger than that in CsI. These nanoscale spatial distributions have been used as the initial configurations of the self-trapped excitons in the kinetic Monte Carlo simulations to understand the nonlinear photon response of inorganic scintillators.

Nuclear Fuel Cycle Safeguards

Philip Casey Durst, Jon R. Phillips, Norman C. Anheier, Jake Benz, Bryan T. Broocks, Bruce A. Bushaw, Luke W. Campbell, Larry Chilton, Matthew M. Conrady, David C. Gerlach, Steven D. Miller, Khris B. Olsen, Mark C. Phillips, Jennifer J. Ressler, Eric Smith, Jennifer E. Tanner

◆ 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 as well as 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. ◆

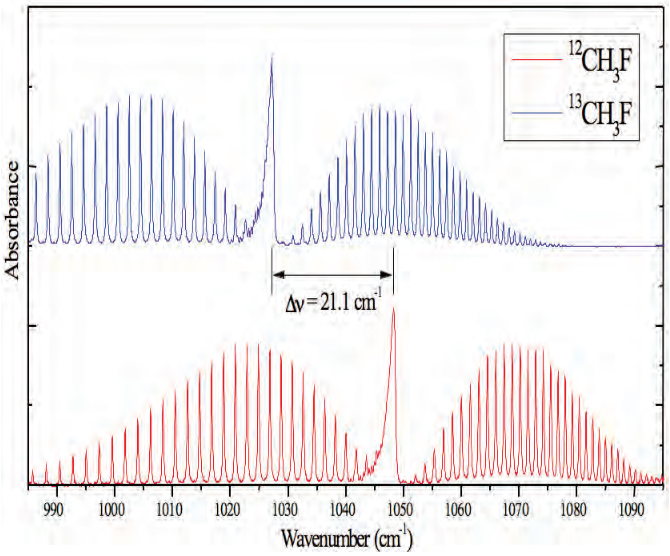
The objective of this project is to develop PNNL's capability to enhance all aspects of the growing nuclear fuel cycle material safeguards in the United States and the world at large. This project addresses the major categories of interest to enhance the safeguards of nuclear material in the worldwide nuclear fuel cycle: improve the safeguarding of nuclear fuel reprocessing, detect undeclared uranium enrichment, enhance the tamper resistance of secured enclosures for safeguards equipment, and reconstruct 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/NNSA policy in support of enhanced nuclear material safeguards and furthering U.S. policy on the non-proliferation of states having nuclear weapons.

High-Energy Coincidence Spectroscopy (HECS) for Spent Fuel Assay. The overall objective in this task is to assess the viability, strengths, and limitations of HECS as a spent fuel assay technique. The first step in meeting this objective is to develop a modeling framework that can be used to perform "virtual" fuel assay using coincidence spectroscopy methods. In FY 2008, methods and software have been developed to perform the following:

- Calculate the isotopic inventory of pressurized-water-reactor fuels with a range of burn-ups representative of today's commercial fleet.
- Use PNNL's Coincidence Lookup Library to define the gamma-ray signatures emitted by each isotope and develop new algorithms to capture the angular correlation of gamma-ray cascades.
- Couple the isotope-by-isotope source term to a Monte Carlo model of the spent fuel assembly surrounded by an array of high-resolution gamma-ray spectrometers.
- Simulate instrument response to each isotope and build a library of isotopic responses that can be drawn to emulate fuel assay in a flexible and computationally efficient manner.
- Validate coincidence spectroscopy analysis algorithms by demonstrating that simulated instrument responses can be used to calculate accurately the original isotopic activity.

With these tasks completed, PNNL now has the ability to simulate the complex and intense background radiation fields emitted by spent fuel assemblies. The next step is to simulate the "signal" created upon actively interrogating the spent fuel assembly with a neutron beam to induce fission in the fissile isotopes. In FY 2009, that software will be able to predict the short-lived fission product inventory and coincidence spectroscopy signatures collected in a virtual assay of realistic spent fuel. The signal extraction and analysis methods developed in FY 2008 will ultimately translate the gamma-gamma spectroscopy data into a fission product yield curve into equivalent ^{239}Pu and ^{235}U. The project will culminate in a comparison of predicted HECS performance in terms of fissile-mass accuracy and precision to the baseline fuel verification technologies of today.

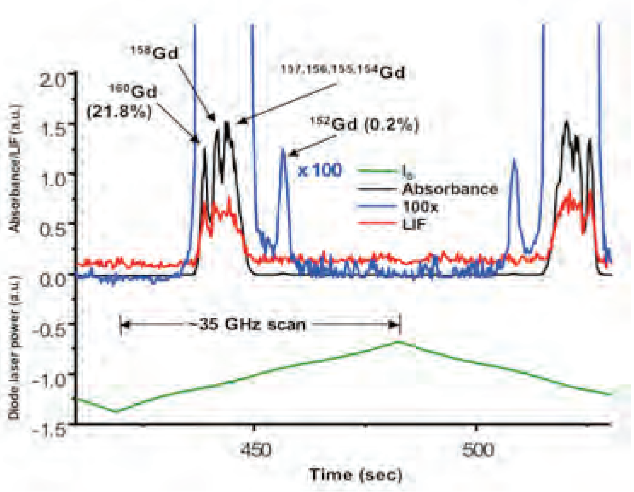
Uranium Hexafluoride Safeguards Monitoring. This task focused on an environmental sampling and analysis concept that targets uranyl fluoride (UO_2F_2) produced in the atmospheric by hydrolysis of fugitive uranium hexafluoride (UF_6)



Uranium Hexaflouride Safeguards Monitoring. *Absorbance spectra of natural and enriched fluoromethane using an infrared external cavity quantum cascade laser. The isotopic-specific spectra is vibrationally-shifted by 21.1 cm^{-1}. While the actual UF_6 shift is smaller (~0.6 cm^{-1}), the fluoromethane study demonstrates the principle of our approach and compels further study using real UF_6 samples.*

process emissions. This approach uses laser vaporization of aerosol particulate samples followed by wavelength-tuned laser diode spectroscopy to characterize the $^{235}U/^{238}U$ isotopic ratio by subtle differences in atomic absorption wavelengths arising from differences in each isotope's nuclear mass, volume, and spin (hyperfine structure for U-235). A laboratory research grade aerosol generator and collector were developed to provide a test bed that facilitates aerosol particle generation and characterization. Additional preparations were made to begin experimental validation of this safeguards monitoring concept starting in FY 2009.

A state-of-the-art miniature ablation laser was identified and procured. We evaluated commercially available stabilized laser diode incorporating a volume holographic grating, an excellent source for uranium isotope measurements. These latest generation laser sources have reduced size and cost by an order of magnitude, enabling future development of compact, onsite, near real-time safeguards monitoring systems. In FY 2009, we plan to conclude the UF_6 investigation by completing measurements on isotopically enriched CO_2 and then submit a journal paper outlining our results. We will also demonstrate the aerosol collection and isotopic measurement concept using UO_2F_2 surrogate materials. We anticipate that the results of our investigations will show 1) UF_6 enrichment measurements can be performed on site in header pipes and storage containers with sufficient sensitivity and accuracy, and 2) UO_2F_2 measurements can be performed continuously onsite using aerosol collection and analysis, effectively replacing monthly manual swipe sampling events that are manpower intensive (subject to collection variability) and require offsite analysis.



HEU Safeguards Monitoring. *Time-resolved isotope absorbance measurements performed by our team on an early project using Gadolinium (uranium surrogate). Single-shot detection sensitivities in the low picogram range (for the minor isotope) and isotope ratios with relative accuracy better than ±10% were demonstrated. The ability to measure accurately the Gd-152:Gd-160 ratio indicates that measurements of U-235:U-238 isotopic ratios for natural (0.72%), depleted (0.25%), and enriched uranium samples will be feasible.*

Beryllium (Be) Trace Separation from Reactor Graphite. This task involved analytical methods development and a start at confirming the main hypothesis:

- Two different schemes for separating and isolating Be from the graphite sample matrix were developed and refined: one for Be only and the other with an established separation for actinide elements so that Be, U, thorium (Th), and Pu can be separated and analyzed from the same sample piece. Chemical yields through each separation are reasonably good.
- A tracer containing ^{10}Be was calibrated for use in precise Be concentration analyses.
- Graphite samples remaining from a previous project study were prepared, and separated Be was analyzed by secondary ionization mass spectrometry (SIMS).
- As predicted by theory, ^{9}Be/^{10}Be ratios were found to be constant in samples spanning a range of neutron fluence exposures.
- Both ^{9}Be and ^{10}Be concentrations in ppb were found to be slightly lower in the samples than predicted.

Work in this task for FY 2009 is expected to include the following:

- Analyses of Be ratios and contents in samples from a higher power reactor that have had higher neutron fluence exposure, which should further confirm constant Be isotope ratios. Concentrations of Be in these samples will reveal either a near linear trend of increasing concentrations in the graphite with fuel burn-up or other effects, such as multi-stage reactions.
- Separate Be from selected low- and high-fluence samples to obtain confirming measurements of Be concentrations by accelerator mass spectrometry, which has been used to measure low levels of 10 Be in environmental samples.
- Prepare standards made from known implanted amounts of Be in high purity graphite to evaluate the feasibility of direct SIMS analysis methods, circumventing more costly and time-consuming chemical exchange procedures.
- Perform uncertainty analysis of Pu yields predicted from Be measurements and compare to known reactor history or other studies that have used other impurity elements.

Container Verification Using Optically Stimulated Luminescence (OSL) Materials in Coatings. This task proposes to develop an OSL coating material that can be applied to the outside surfaces of enclosures such as nuclear material containers, safeguards equipment cabinets, surveillance camera housings, and detector cable conduit. The project was initiated with the purchase of powder coating paints, a powder coating applicator gun, and the processing of infrared-grade lithium fluoride (LiF) OSL powder. Polymer and powder handling expertise was identified within PNNL, and the OSL phosphor materials were blended with various colors of powder coating materials. An off-white color was initially selected due to its minimal absorbance of both the excitation and OSL emission light.

Several different grinding techniques were tested, and various solvents were used in an attempt to blend the small grain-size OSL phosphor with the powder paint without causing the very small OSL particles to agglomerate. Grinding the LiF OSL crystals is straightforward, but the very small particles tend to stick together in clumps due to very strong dipolar charges unique to LiF. Most alkali-halides develop surface charges when ground to micron particle size, but the unique nature of LiF bonding exacerbates the agglomeration problems. Several techniques for mixing the ground OSL phosphor with the powder coatings pigments were tested before a successful formulation was developed. Certain solvents help “wet” the OSL phosphor surfaces and prevent agglomeration, enabling the powder coating pigment to be introduced without clumping.

Clever selection of optical filters and readout techniques vastly increases the signal-to-noise (SNR) ratio and enables the OSL research team to measure easily the OSL emission light in the very large background of unwanted fluorescence signal from various sources. Several OSL phosphor materials have been developed, but LiF was selected for this project due to its fast fluorescent decay and the multiple OSL emission peaks in the green, red, and infrared.

A Fuji ultraviolet/infrared camera has been purchased and will be used to demonstrate the OSL phosphor coating readout with an off-the-shelf camera, which came with a variety of optical filters that will be useful in conditioning the excitation light and OSL emission. In addition to powder paint coatings, the OSL development team has produced thin coatings of fine infrared-active OSL particles mixed with ultraviolet curable polymers. These thin layers could be developed into a spray-can type deployable coating or as part of an overcoating of the typical powder coating process.

Our OSL research team has made excellent progress during FY 2008 in demonstrating practical OSL coating technology and the readout of the OSL coatings with high SNR.

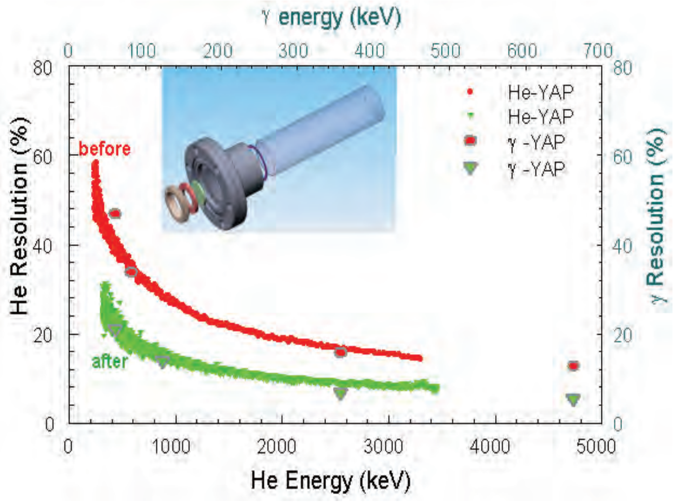
Response of Radiation Detector Materials to Ions

Yanwen Zhang, Brian D. Milbrath

◆ This project will demonstrate combinatorial fast screening techniques in obtaining quantitative and relevant data on the response of candidate radiation detector materials (thin films or single crystals) to energy deposition. The results will provide validation data for theoretical model predictions and intrinsic material properties relevant to detector performance that will assist and accelerate the discovery or identification of new detector materials. ◆

Recent demands for new radiation detector materials for proliferation detection, treaty verification, safeguards, and crisis management have prompted research efforts on accelerated material discovery. For γ-ray detection and isotope identification, a relatively large high-quality crystal is necessary. Accelerated materials discovery efforts are needed, and fast screening techniques are therefore required to investigate numerous candidate materials to provide information about material properties relevant to detector performance.

Historically, the discovery of new inorganic scintillators has been slow due to the difficulties inherent in large crystal growth. Various film deposition techniques have been advanced, and high-quality thin films of candidate materials can be readily produced by various modern growth techniques. Based on single excitation, an ion technique is applicable to thin films or small crystals. For light ions (H or He), the ion-solid interaction is predominantly by electronic energy transfer, and light of a characteristic spectrum is emitted following radiation absorption. The photon yield and energy resolution can be investigated as a function of radiation energy, which provides intrinsic information on the material radiation response and is therefore used to identify potential gamma detector candidates.



Energy resolution as a function of ion energy for the YAP crystal before and after the system improvement (shown as inset). Gamma results are also included for comparison.

For gamma detection, a solution might be synthesizing nanocomposites, which would combine high sensitivity, efficiency, and good energy resolution with large available size and manufacturability. To establish the ion technique, we have also investigated ion-nanoparticle interactions for radiation detection. The physical nature of quantum dots has a significant impact on luminescence response. Studies on ion-induced luminescence were performed to achieve a fundamental understanding on scintillation physics of ion beam-nanoparticles interactions in quantum dot structures. Instead of a PMT, fiber optics is used to guide signals into a spectrograph followed by a CCD. LaF_3:$Ce^{3+}Tb^{3+}$ nanoparticles ($La_{0.4}Ce_{0.45}Tb_{0.15}F_3$) in poly-vinyl-alcohol were investigated. The CeF_3 nanoparticles doped with a Tb^{3+} ion show a strong green emission under both 250 nm photon excitation and 2.0 MeV He ion irradiation. Similar emission profiles are observed that both consist of the characteristic emission of Tb^{3+} with the $^5D_4$-$^7F_5$ transition with 542 nm being the most prominent group.

During FY 2008, we achieved the following:

- Validated that TOF-detector setup is an efficient, fast screening technique for studying both semiconductors and scintillators (including both crystals, polycrystals, and nanoparticles).
- Identified nonlinearity in low-energy regions for Si detector attributed from the tendency for heavy ions to lose energy by means other than electronic collisions (nuclear stopping).
- Examined different benchmark scintillating materials (CaF_2, CsI:Tl, YAP, BGO, and plastic scintillators); relative light yield and energy resolution trends are consistent with known properties of these materials from gamma tests.
- Improved the experimental set up where the energy uncertainty is reduced from ~10% down to ~1% for the scintillation measurements.
- Investigated emission spectra from photoluminescence and ion-induce luminescence from different scintillation materials, which reveals the underlying scintillation physics for radiation detection applications.

Spent Fuel Shipping and Storage Cask Monitor

Morris S. Good, Philip Casey Durst, James R. Skorpik, David W. Wootan, Bruce E. Watson

◆ A labor-saving and cost-effective system is desired to ascertain the continuity of knowledge of spent nuclear fuel (material) stored within a dry storage cask or container. Our concept was to implement data logging and the remote monitoring of individual containers. ◆

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 expected to escalate the generation and storage of material. 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. A method that improves the practice of ascertaining material continuity of knowledge while reducing inspector labor and radiation exposure will be needed. If designed and implemented sensibly, the following advantages would be achieved:

- dramatic improve in the rate at which material continuity of knowledge state is ascertained
- monitor containers during transit and interim storage
- flag a change (if detected) and enable a timely response
- increase inspection efficiency, reduce inspector exposure to radiation, and reduce labor
- reduce intrusiveness to nuclear facility operation.

Material containment and surveillance has been used by the International Atomic Energy Agency (IAEA) to maintain the continuity of knowledge on material accepted for inspection under a country's Comprehensive Safeguards Agreement. Monitoring technologies combined with host nation declarations and physical inspections provide the basis to draw independent conclusions about material location and status. Currently, IAEA inspectors apply seals to containers and periodically conduct onsite visits to inspect these seals. The timeliness of the inspection rate is dependent on fuel characteristics and is typically a 12-month period.

Past efforts include 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. Several technology gaps for a container monitor are an integrated complement of sensors specific to spent nuclear fuel and attachment of the sensor package to a diverse set of container-overpack assemblies. Project work for this first year primarily addressed potential sensing technologies for interim storage containers.

Work included a publication and 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 (July 2008), 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 will need to operate.

Desired sensor attributes for the container-overpack sensor module.

Sensor Attribute and Comments	Sensors
Removal of container lid would increase radiation outside the container and permit light (if present) to enter the inner container.	• Optical and/or wire loop seals • Acceleration • Tilt • Light detection within inner container • Increased radiation external to container • Internal gas environment change • Smart bolt, if fasteners used • Weld inspection, if closure weld used
Container movement would cause a localized weight change and would occur at either the concrete pad or overpack.	• Acceleration • Tilt • Localized weight or stress-strain change
Underwater transfer of material is commonly used to provide radiation shielding.	• Hydrostatic pressure • Electrical conductivity • Capacitance
Detection of a machining event could be used to trigger other monitoring activities.	• Vibration • Acoustic emission
Radiation sensors tend to be power intensive devices.	• Gamma and limited neutron radiation outside container • Extreme radiation within container

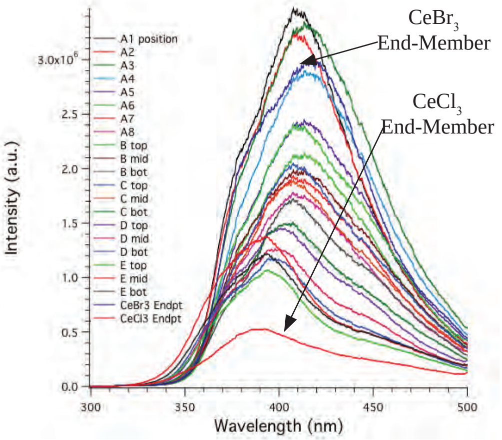
Synthesis and Characterization of Thin Films for Rapidly Screening Detector Materials

Larry C. Olsen, Brian D. Milbrath

◆ Advanced materials are needed to fabricate sensitive solid-state and scintillator detectors to provide security against the illegal entry of radioactive material into the United States. This project is developing screening methods to identify potentially new radiation-detector materials. ◆

The urgent need for improved radiation-detector materials drives the development of rapid screening methods for selecting candidate materials to be used to enhance homeland defense against new terrorist threats and detect and prevent the proliferation of weapons of mass destruction. Although many measurements can provide interesting information about candidate materials, the specific aim of this effort is to develop tools that can be used to screen potential detector materials rapidly. Material synthesis, semiconductor film characterization, and scintillator film characterization are key components of this project. Materials synthesis primarily involves using thin-film deposition systems based on sputtering and electron beam deposition. PNNL's broad base of experience in the areas of radiation detection and with semiconductor devices and characterization is being used to develop rapid screening methods for evaluating materials for potential scintillators and semiconductor devices for gamma-ray detection.

Under this project, we expect to: 1) demonstrate that thin films deposited onto appropriate substrates by sputtering can be used to select candidate detector materials for solid-state detectors and scintillators, 2) establish measurement procedures that can characterize the potential of semiconductor materials for gamma-ray solid-state detectors in a timely manner, 3) establish measurement procedures that can characterize the potential of scintillator materials for gamma-ray detection in a timely manner, and 4) successfully apply PNNL-developed rapid screening procedures to new detector materials.



PL intensity versus wavelength for a series of $CeCl_3/CeBr_3$ *thin films obtained with combinatorial deposition runs. Intensity increases as the value of x increases from 0 to 1 to* $CeBr_3/CeCl_3$*) as films.*

To validate the approach outlined for rapid screening, initial studies were conducted on established detector or reference materials. Silicon and cadmium telluride (CdTe) were selected as reference semiconductors, while Eu^{2+} doped calcium fluoride (CaF_2) was selected as the reference scintillator, though most semiconductor studies have been devoted to CdTe. The electronic and physical properties of CdTe films grown by sputtering and physical vapor deposition have been evaluated. Because deposited and post-heat treated (with cadmium chloride) films were studied, electron mobilities of films subjected to post-heat treatment were estimated at 800 $cm^2/V/s$, which compares favorably with values determined for single crystal CdTe; thus, in the case CdTe, we showed that thin films could be used for screening purposes. One key conclusion from the study is that in order to evaluate the potential of a semiconducting material for a detector, it is important to have grain sizes on the order of one micron.

Eu^{2+}-doped CaF_2 was studied as a reference scintillator material. These films were deposited by electron beam deposition. Characterization has involved crystal structure determination with grazing incidence x-ray diffraction, composition analysis with x-ray photon spectroscopy and energy-dispersive spectrometry, and alpha- and photo-luminescence measurements. Films were confirmed to have the appropriate crystal structure. Further, the maximum luminescence was emitted for a doping level of 0.2% Eu^{2+}, and luminescence lifetimes were less than 1 microsecond. Both of these results agree with the information for commercially available materials, thereby suggesting that thin films can be used to screen new scintillator materials.

During FY 2008, activities focused on the development of rapid screening procedures for scintillators. Combinatorial deposition studies of $CeBr_3$ and $CeCl_3$ were carried out using two thermal evaporation sources. Since cerium halides are hygroscopic, samples must be handled accordingly during transfer, storage, and analysis. SEM and energy-dispersive spectrometry were used for film microstructure and compositional measurements, x-ray diffraction was used to determine crystal structure and crystallite size, and photo-luminescence measurements were conducted to obtain a measure of "brightness." Samples used for photoluminescence and x-ray diffraction studies were protected from moisture exposure during transfer and analysis using polymer/oxide multilayer barrier coatings using a PNNL-developed deposition process.

Theoretical Modeling and Ex-Reactor Testing of Fuel Properties to Accelerate Fuel Qualification

Carl E. Beyer, Brady Hansen, Andrew Casella, Rick E. Williford, Ken J. Geelhood

◆ This effort is intended to shorten the fuel development and qualification time by providing better data early in the process as opposed to waiting for the completion of lengthy irradiation test campaigns. ◆

There is renewed interest in the U.S. in expanding its use of clean, safe nuclear power for domestic needs and there are signs that the rest of the world is considering the expansion of nuclear power as part of an effort to meet its growing energy needs while minimizing CO_2 emissions. The recent Global Nuclear Energy Partnership (GNEP) program bears witness to this renewed interest 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. The reactors being considered under the GenIV initiative include the Very-High-Temperature Reactor (VHTR) and Supercritical-Water-Cooled Reactor (SCWR) which offer greater overall efficiencies and enable the production of hydrogen for use in the transportation industry, and the Gas-Cooled (GFR), Lead-Cooled (LFR), and Sodium-Cooled (SFR) fast reactors.

Fuels used in any new reactor types being considered by the DOE will need to be qualified so that they can be licensed for use by government or commercial entities. This research is focused on two goals to assist in accelerating the qualification of new fuel types for new reactors: 1) demonstrate PNNL's capability to model fuel performance based on present available theoretical knowledge, and 2) fabricating simulated RADFUEL to perform material property measurements of new simulated fuel types. The latter will assist in proving that the theoretical modeling is valid. This project is intended to reveal PNNL's ability to accelerate fuel development and qualification for transuranic fuel that is to be burned in the proposed advanced recycle reactor; however, the methods developed could be applied to various fuel types and forms in support of the development of other fuel and reactor types.

The first goal of the project will result in a theoretical model for fuel thermal conductivity for mixed oxide (MOX) containing minor actinides; the second 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 the advanced fuels at various burn-up conditions to support performance modeling needs in advance of reactor testing. While the initial focus will be on oxide fuels, the methodology and processes developed may be expanded for other fuel types. These data and model developments will advance the modeling efforts for new fuel types. A paper on the theoretical thermal conductivity model was written and presented at the ANS Annual Meeting in Anaheim, CA (June 2008) and published in the transactions. This report demonstrated that the model can successfully predict thermal conductivity for several oxide fuel types (unirradiated condition) with different additives based on comparisons with data from the literature.

Origin calculations were performed to examine the fission product differences between UO_2 and MOX fuel in light water reactors and MOX fuel with actinides in FRs. During FY 2009, these results will be used to develop the impact of irradiation on fuel thermal conductivity of MOX with actinides in FRs, with the results submitted for publication.

Fabrication and measurement activities focused on procuring and modifying the equipment necessary for pellet fabrication to perform measurements. Initial testing of fuel pellet fabrication was performed to optimize parameters so that the PNNL-fabricated fuels have similar properties (density, porosity, grain size) as commercially-procured pellets. A Netzsch Laser Flash Analyzer (LFA) to be used for measuring the thermal diffusivity of RADFUELs and other simulants was modified for installation in a radiologic fume hood (to be completed in early FY 2009). Similarly, modifications and upgrades to a Netzsch STA 409 thermal analyzer have been made to measure the heat capacity of radioactive samples. Both instruments are capable of measuring these properties over a wide range of temperatures, including up to nominal reactor operating temperatures. During FY 2009, the primary activities will be to perform measurement tests of commercially procured fuels to establish a baseline, to fabricate Gd-doped fuels and RADFUEL, and to determine the thermal conductivity of these fabricated fuels. The measurement results of thermal conductivity will be submitted for publication.

Modified LFA (for thermal conductivity measurement) ready to be installed in the radiological fume hood behind it.

Physics

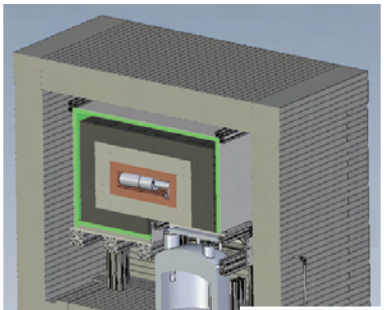
First Operation of a Novel, High-Mass Detector as a Weakly Interacting Massive Particle (WIMP) Dark Matter Detector

Marty E. Keillor, John L. Orrell

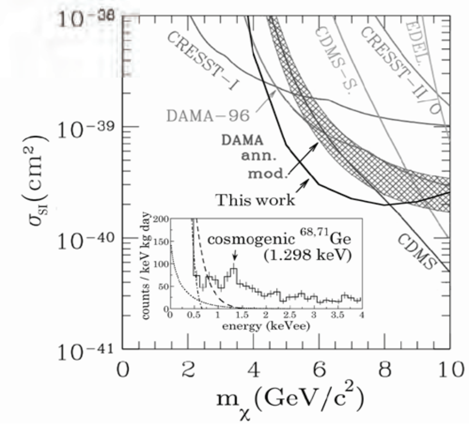
◆ Direct detection of dark matter particles is perhaps the single most pressing astroparticle physics measurement sought by cosmologists and theoretical particle physicists alike. Theoreticians postulate the existence of a weakly WIMP, the gravitational influence of which is ubiquitous but otherwise does not participate in the familiar interactions of the standard model of particle physics. ◆

Experimental searches for WIMP dark matter span a decade, dove-tailing on cosmologists' efforts to account for the discrepancy between the amount of visible mass in the universe with observed gravitational effects that indicate 95% of the universe mass is in fact unseen. This project is based on recognition of an advance in low-energy threshold (~0.3 keV) germanium detector technology that can exploit the exponential increase in WIMP signal by measuring decreasingly energetic nuclear scattering recoils. This project takes timely advantage of access to such a high-mass (~0.5 kg) germanium detector that will be installed and operated at an underground location and assessed as a candidate technology for future large-scale dark matter searches.

a) Low background shield design.



Our project will collect and analyze data covering a low-energy region not previously explored with large high purity germanium spectrometers. The low-energy capability is anticipated to extend down to 0.3 keV, providing a significant increase in the measurable WIMP-nucleus elastic scattering signature. This project 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 will assess this new detector technology for future large-scale WIMP dark matter searches.



b) New dark matter exclusion limits from a low-threshold germanium detector.

A low background detector shield was designed (Figure a), and some of the components were fabricated. The entire shield apparatus was sent to the Soudan Underground Laboratory operated by the University of Minnesota. The detector shield was staged in preparation of assembly and insertion of the low-energy threshold germanium detector used in this project. Initial operation of the low-energy threshold detector showed one unexpected feature and one shortcoming. The unexpected feature was the identification of a population of bona fide detector events that entirely lacked gamma-ray spectroscopic information. These events were readily distinguished via the use of a waveform digitizing data acquisition systems that allowed for pulse shape analysis. While other groups had previously used similar methods, it was not clear whether our extensive examination was artifact or discovery. This detector feature generated interest and has partially delayed deployment of the detector to Soudan. The one shortcoming is the fact that our use of a *stock* wave form digitizing data acquisition system made reaching the anticipated low-energy threshold of 0.3 keV impossible; we are only able to reach 1 keV. It is believed that a software fix provided by the digitizing data acquisition system's manufacturer will overcome this shortcoming. The detector was scheduled for installation at Soudan during the second week of October 2008.

PNNL's efforts have involved us collaboratively on the advancement of dark matter detection in the broader scientific community. A nearly identical detector was installed at a shallow underground location and operated for only 20 days but was able to place new limits on dark matter properties as depicted in Figure b and reported in the *Physical Review Letters* journal.

Integrated Assessment of the Origins of Scintillator Nonlinearity

Bret D. Cannon, Joseph A. Caggiano, Erin A. Miller

◆ Scintillator nonlinearity is a key limitation on the resolution with which gamma-ray energies can be measured by the most common inorganic scintillators. Understanding the mechanisms responsible for scintillator nonlinearity will accelerate the discovery of improved scintillator materials by leading to a predictive theory of what material properties lead to low nonlinearity in scintillators. ◆

Scintillator-based radiation detectors are used extensively for national security applications, including smuggled nuclear weapons detection and key radioactive component materials. Detectors for such applications count the number and measure the energy of each gamma ray that is completely absorbed in the scintillator. The ability of such a detector system to distinguish between benign radiation sources (such as smoke detectors) and possible nuclear weapons material is determined by the detector's energy resolution (i.e., the ability to differentiate between gamma rays of different energies). Better energy resolution can improve the tradeoffs among detection sensitivity, false alarm rates, and measurement speed. The energy resolution of most scintillator materials is substantially degraded by scintillator non-linearity, and the mechanisms responsible for nonlinearity are unknown. Trial-and-error discovery is too inefficient to meet current national security needs for improved radiation detection materials. In addition, the lack of understanding of mechanisms for scintillator nonlinearity is a gap in our basic scientific understanding of ionizing radiation effects in matter. The goal under this project is to determine the mechanisms for nonlinearity that will lead to a predictive theory of what material properties are required for low nonlinearity in scintillators.

We began with a detailed study of the 50 years of previous work on nonlinearity, looking both for evidence constraining possible mechanisms and ideas suggesting new experimental approaches. The most obvious feature of nonlinearity is its near universality in inorganic scintillators: only after 50 years of scintillator discovery and development was a very low nonlinearity inorganic scintillator reported, and it has a light yield half that of thallium-doped sodium iodide [NaI(Tl)]. This nonlinearity feature led us to look for general mechanisms that could produce such a common phenomenon. By contrast, the other major class of gamma-ray detectors and semiconductors show little or no nonlinearity. This difference between scintillators and semiconductors eliminates initial stages of converting gamma-ray energy into free electrons and holes as the source of nonlinearity, since theses stages are essentially the same in both types of materials. There appears to be little or no temperature dependence of nonlinearity based on the limited published data, which covers only five inorganic scintillators but includes most classes studied over a much larger temperature range. This data led us to hypothesize that nonlinearity in all inorganic scintillators is essentially independent of temperature, which would significantly constrain possible mechanisms and eliminate all nonlinearity mechanisms requiring the use of thermal energy.

These features led us to consider a new class of mechanisms for nonlinearity involving free electrons cooled below the threshold needed to create more free electrons and holes but not cooled enough to be trapped. All free electrons produced from a gamma-ray's energy pass through such a stage. Such electrons have their largest concentration after the initial stages of the energy cascade and would be consistent with the differing behaviors of semiconductors and scintillators. These electrons have enough energy that they would not be dependent on thermal energy for participating in reactions, which would be consistent with little or no temperature dependence.

We used semi-classical modeling to study the timescale and transport of these electrons in crystals as they cool to thermal energies by scattering from phonons, which are vibrations of the crystal lattice. According to our modeling, such electrons can travel up to 1000 nanometers in NaI(Tl), take up to 2 picoseconds to cool, and ends the diffusive type path typically 10 to 50 nanometers from the start. Semi-classical modeling of such processes gives lower limits of the cooling times and distances because the calculated rates are much faster than the rate of loss of quantum coherence, which violates the assumed independence of successive scattering events. Our modeling results are consistent with femtosecond laser measurements in similar crystals of the time for the appearance of optically absorbing states with which these electrons could react. Thus, these hot electrons are a plausible key intermediate in the reactions producing nonlinearity.

We also tested the hypothesis that different optical emission pathways could lead to nonlinearity. We measured the optical emission spectra of thallium-doped cesium iodide CsI(Tl) using for excitation gamma-rays of different energies that correspond to different parts of the nonlinearity curve. Our results rule out this hypothesis playing any significant role in the nonlinearity of CsI(Tl).

Phase Contrast X-Ray Imaging for Enhanced Explosives Detection

Erin A. Miller, H. Allen Siefert

◆ 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. This research will verify a new technique for performing phase contrast imaging and evaluate the efficacy of the technique for the detection of highly concealed explosives. ◆

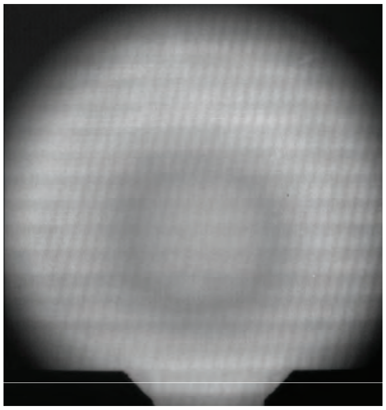
Phase contrast is similar to conventional X-ray imaging, but image contrast is produced by local variations in the object's X-ray index of refraction rather than its absorption. The technique has been used for several years with synchrotron X-ray sources, where it has been of use for imaging low-density and -*Z* samples, such as biological specimens or polymers. Operational applications incompatible with synchrotron sources have been limited due to stringent source coherence requirements. In this approach, a series of gratings is used to improve the X-ray source characteristics, set up an X-ray interference pattern sensitive to distortions in the X-rays, and detect those fine distortions. This raises 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.

Important progress in FY 2008 has included the detection of a phase contrast signal and improved gratings fabrication techniques. At the end of FY 2007, a new iteration of gratings was tested using the phase contrast testbed at HFHS. Moiré fringes were observed, produced by the combination of the phase and analyzer gratings. Further study indicated that the fringes were due to an X-ray interference pattern produced at the phase grating. Since the contrast mechanism that produces Moiré fringes is the same as that which produces a phase contrast image, we can test system sensitivity to alignment and optimize contrast. While the fringe pattern itself (in period and orientation) is sensitive to the analyzer alignment phase grating when rotated about the beam axis, and spacing due to magnification effects, contrast seemed only weakly dependent on most system alignment parameters. This indicates that the setup is relatively robust, an important consideration for future applications. This conclusion was supported by analytic calculations of the optics of the phase and analyzer gratings, which also indicate robust behavior.

Although phase contrast was observed, the contrast level was insufficient to support imaging; at a shorter working distance (with a different source grating), no fringes were seen at all. While higher flux would improve signal-to-noise, SEM images of the gratings indicate that there is significant room for improvement. In particular, moving to higher energies required by many applications will require much thicker gratings to achieve the same interaction. For this reason, investigating grating fabrication techniques has become an important component of our work.

An improved version of the source grating was obtained from the Washington Technology Center, which fabricated the first two sets of gratings. The phase grating appears to be of high quality, so no further attempts were made. For the analyzer grating, the fine spatial size (2 μm period) mandated by the interference pattern spacing and the large depth (at least 10 μm) required to attenuate the X-rays make fabrication extremely difficult. Two different design options were pursued, along with a variety of techniques, including sputtering (on two different systems), electro-plating (with two different plating baths), thick film photo-resist, and LIGA. Sputtering did not result in a sufficiently uniform gold deposition. Thick film photoresist is promising but may have stability issues at high-aspect ratios. LIGA may suffer similar issues, but the photoresist is generally more stable than typical lithography. We anticipate the results of these efforts early in FY 2009.

Work in FY 2009 will focus on completing the next round of grating fabrication followed by a set of X-ray measurements to test new gratings. The emphasis will shift towards imaging, moving from simple objects to more complex environments to evaluate the influence of clutter in a phase contrast image. Finally, work will continue toward developing new data processing algorithms.



White field image with Moiré fringes (diagonal lines from lower left to upper right). Horizontal lines are due to uneven illumination; scintillator holder is dark shape at bottom.

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 properties 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 $0\nu\beta\beta$ decay energy of 2039 keV per ton of active detector mass per year. This is a factor of 100 lower than previous generation experiments and 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.

The expected research capabilities developed under this project will address significantly more challenging purity requirements, including the unprecedented purity levels needed in neutrinoless double-beta decay and dark matter experiments. The outcome of this research will be the development of a capability to produce ultra-pure copper parts of the desired mechanical properties and radiological purity of interest to future basic science programs. Our results will enable the laboratory to build the necessary capabilities of interest to the Majorana collaboration and the broader low-background physics community.

The following project milestones occurred during FY 2008:

- Procurement using non-LDRD funds and initial setup of an electroanalytical system was completed. Also, new electronics for the PNNL ultra-low background detector were procured.
- Construction and initial setup of a large-scale electroforming apparatus was completed.

During FY 2009, we have the following project activities planned:

- Setup a portable clean room, and perform a complete setup of faraday cage and electrochemical cells in the portable clean room.
- Install ULB detector electronics and bring the detector online (other funding).
- Evaluate materials background on ULB and prepare for 228Th tracer studies.
- Conduct 228Th studies under varying contaminant concentrations and current conditions.
- Install large-scale electroforming apparatus into the portable clean room, complete acid leaching processes, and conduct electroforming on a large-scale SS mandrel to test scaling parameters.
- Evaluate the purity of copper produced from a large-scale system.

Among the several technical challenges 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.

This project will be addressing much larger electroformed copper parts and much more stringent radiopurity requirements than prior work. PNNL is the science leader in this area and is best positioned to achieve these challenging goals. 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 2008 Refereed Publications

Appendix A
Fiscal Year 2008 Refereed Publications

During FY 2008, PNNL's LDRD Program resulted in 108 refereed publications. These journal articles, book chapters, and select conference papers are listed below in alphabetical order by the author's last name.

Ansong CK, H Yoon, AD Norbeck, JK Gustin, JE McDermott, HM Mottaz, J Rue, JN Adkins, F Heffron, and RD Smith. 2008. "Proteomics Analysis of the Causative Agent of Typhoid Fever." *Journal of Proteome Research* 7(2):546-557.

Bachelor PP, JI McIntyre, JE Amonette, JC Hayes, BD Milbrath, and P Saripalli. 2008. "Potential Method for Measurement of CO_2 Leakage from Underground Sequestration Fields Using Radioactive Tracers." *Journal of Radioanalytical and Nuclear Chemistry* 277(1):85-89.

Belov ME, BH Clowers, DC Prior, WF Danielson, III, AV Liyu, BO Petritis, and RD Smith. 2008. "Dynamically Multiplexed Ion Mobility Time-of-Flight Mass Spectrometry." *Analytical Chemistry* 80(15):5873-5883.

Boyles KR, SM Chajkowski, RS Disselkamp, and CHF Peden. 2006. "An Examination of the H/D Isotope Substitution Effect on Selectivity and Activity in the Cavitating Ultrasound Hydrogenation of Aqueous 3-buten-2-ol and 1,4-pentadien-3-ol on Pd-black." *Industrial and Engineering Chemistry Research* 45(11):4015-4018.

Buchko GW, O Litvinova, H Robinson, AF Yakunin, and MA Kennedy. 2008. "Functional and Structural Characterization of DR_0079 from Deinococcus radiodurans, A Novel Nudix Hydrolase with a Preference for Cytosine (Deoxy) Ribonucleoside 5'-di- and Triphosphates." *Biochemistry* 47(25):6571-82.

Buchko GW and HJ Sofia. 2008. "Backbone 1H, 13C, and 15N NMR Assignments for the Cyanothece 51142 Protein cce_0567: A Protein Associated with Nitrogen Fixation in the DUF683 Family." *Biomolecular NMR Assignments* 2:25-28.

Chase JM, KL Schuchardt, G Chin Jr, JA Daily, and TD Scheibe. 2008. "Iterative Workflows for Numerical Simulations in Subsurface Sciences." In *Proceedings of 2008 Institute of Electrical and Electronics Engineers Congress on Service Part 1*, pp. 461-464. Institute of Electrical and Electronics Engineers Computer Society, Los Alamitos, California.

Chavarría-Miranda D, A Marquez, J Nieplocha, KJ Maschhoff, and C Scherrer. 2008. "Early Experience with Out-of-Core Applications on the Cray XMT." In *Institute of Electrical and Electronics Engineers International Symposium on Parallel and Distributed Processing*, IPDPS 2008, pp. 2379-2386. Institute of Electrical and Electronics Engineers, Piscataway, New Jersey.

Chavarría-Miranda D, J Nieplocha, C Scherrer, HJ Sofia, A Marquez, and DK Gracio. 2008. "Cray XMT Brings New Energy to High-Performance Computing." *SciDAC Review* Fall 2008(9).

Cheng TY, DJ Szalda, JC Hanson, JT Muckerman, and RM Bullock. 2008. "Four-Electron Donor Hemilabile n3-PPh3 Ligand that Binds Through a C = C Bond Rather than an Agostic C-H Interaction, and Displacement of the C = C by Methyl Iodide or Water." *Organometallics* 27(15):3785-3795.

Chin G, Jr, DK Gracio, and AR Chappell. 2007. "Concept-Based User Interfaces." In *McGraw Hill 2008 Yearbook of Science & Technology*, pp. 79-83.

Chin MH, W Qian, H Wang, VA Petyuk, JS Bloom, DM Sforza, G Lacan, D Liu, AH Khan, RM Cantor, DJ Bigelow, WP Melega, DG Camp, II, RD Smith, and DJ Smith. 2008. "Mitochondrial Dysfunction, Oxidative Stress and Apoptosis Revealed by Proteomic and Transcriptomic Analyses of the Striata in Two Mouse Models of Parkinson's Disease." *Journal of Proteome Research* 7(2):666-677.

Daly DS, KK Anderson, EA Panisko, SO Purvine, R Fang, ME Monroe, and SE Baker. 2008. "A Mixed-Effects Statistical Model for Comparative LC-MS Proteomics Studies." *Journal of Proteome Research* 7(3):1209-1217.

Ding SJ, B Wang, JM Jacobs, W Qian, F Yang, AV Tolmachev, EF Strittmatter, RJ Moore, ME Monroe, SO Purvine, Q Luo, KM Waters, DG Camp, II, RL Klemke, and RD Smith. 2008. "Quantitative Phosphoproteome Analysis of Lysophosphatidic Acid Induced Chemotaxis Applying Dual-Step ^{18}O Labeling Coupled with Immobilized Metal-Ion Affinity Chromatography." *Molecular & Cellular Proteomics (MCP)*. [In press]

Dresel PE, KB Olsen, JC Hayes, JI McIntyre, SR Waichler, and BM Kennedy. 2008. "Environmental Applications of Stable Xenon and Radioxenon Monitoring." *Journal of Radioanalytical and Nuclear Chemistry* 276(3):763-769.

Duckworth DC, M Liezers, SA Lehn, and M Douglas. 2008. “Electrochemically-Modulated Separation and Mass Spectrometric Analysis of Actinides in Difficult Matrices.” In *INMM 8th International Conference on Facility Operations-Safeguards Interface*. PNNL-SA-61492, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Eustis S, D Radisic, KH Bowen, RA Bachorz, M Haranczyk, GK Schenter, and MS Gutowski. 2008. “Electron-Driven Acid-Base Chemistry: Proton Transfer from Hydrogen Chloride to Ammonia.” *Science* 319(5865):936-939.

Fan PD, M Valiev, and K Kowalski. 2008. “Large-Scale Parallel Calculations with Combined Coupled Cluster and Molecular Mechanics Formalism: Excitation Energies of Zinc-Porphyrin in Aqueous Solution.” *Chemical Physics Letters* 458(1-3):205-209.

Ferris KF, BJM Webb-Robertson, DV Jordan, and DM Jones. 2008. “Data-Driven Exploration of the Ionization-Phonon Partitioning in Scintillating Radiation Detector Materials.” In *Institute of Electrical and Electronics Engineers Transactions on Nuclear Science* 55(3:2):1042-1048. Institute of Electrical Electronics Engineers, Piscataway, New Jersey.

Gallavardin SJ, KD Froyd, U Lohmann, O Moehler, DM Murphy, and D Cziczo. 2008. “Single Particle Laser Mass Spectrometry Applied to Differential Ice Nucleation Experiments at the AIDA Chamber.” *Aerosol Science and Technology* 42(9):773-791.

Gallavardin SJ, U Lohmann, and DJ Cziczo. 2008. “Analysis and Differentiation of Mineral Dust by Single Particle Laser Mass Spectrometry.” *International Journal of Mass Spectrometry* 174(1-3):56-63.

Gao F, LW Campbell, YL Xie, R Devanathan, AJ Peurrung, and WJ Weber. 2008. “Electron-Hole Pairs Created by Photons and Intrinsic Properties in Detector Materials.” In *IEEE Transactions on Nuclear Science* 55(3):1079-1085.

Gatchel JR, K Watase, C Thaller, JP Carson, P Jafar-Nejad, CA Shaw, T Zu, HT Orr, and HY Zoghbi. 2008. “The Insulin-Like Growth Factor Pathway is Altered in Spinocerebellar ataxia Type 1 and Type 7.” In *Proceedings of the National Academy of Sciences of the United States of America* 05(4):1291-1296.

Gibson TD, KL Schuchardt, and EG Stephan. 2008. “Application of Provenance for Automated and Research Driven Workflows.” In *Second International Provenance and Annotation Workshop*. ™PNNL-SA-59702, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Gorton I. 2008. “Software Architecture Challenges for Data Intensive Computing.” In *WICSA 2008*: *Proceedings of the 7th Working IEEE/IFIP Conference on Software Architecture*, February 18-22, 2008, Vancouver, British Columbia, Canada, pp. 4-6. IEEE Computer Society, Los Alamitos, California.

Gorton I, AS Wynne, JP Almquist, and J Chatterton. 2008. “The MeDICi Integration Framework: A Platform for High Performance Data Streaming Applications.” In *WICSA 2008: Proceedings of the 7th Working IEEE/IFIP Conference on Software Architecture*, February 18-22, 2008, Vancouver, British Columbia, Canada, pp. 95-104. IEEE Computer Society, Los Alamitos, California.

Greitzer FL. 2008. “Methodology, Methods and Metrics for Testing and Evaluating Augmented Cognition Systems.” Chapter 6 in *Augmented Cognition: A Practitioner's Guide*, ed. DD Schmorrow and KM Stanney, pp. 144-174. Human Factors & Ergonomics Society, Santa Monica, California.

Greitzer FL and DH Andrews. 2008. “Training Strategies to Mitigate Expectancy-Induced Response Bias in Combat Identification: A Research Agenda.” In *Human Factors Issues in Combat Identification Workshop*. Air Force Research Laboratory, Mesa, Arizona.

Greitzer FL, AP Moore, DM Cappelli, DH Andrews, L Carroll, and TD Hull. 2008. “Combating the Insider Cyber Threat.” *IEEE Security & Privacy* 6(1):61-64.

Greitzer FL, R Podmore, M Robinson, and P Ey. 2008. “Naturalistic Decision Making for Power System Operators.” In *The 9th Bi-Annual International Conference on Naturalistic Decision Making*. PNNL-SA-62694, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Greitzer FL, A Schur, ML Paget, and RT Guttromson. 2008. “A Sensemaking Perspective on Situation Awareness in Power Grid Operations.” In *IEEE Power and Energy Society General Meeting – Conversion and Delivery of Electrical Energy in the 21st Century*, pp. 1-6.

Hardy JS, EC Thomsen, NL Canfield, JV Crum, KS Weil, and LR Pederson. 2007. “Development of Passive Hydrogen Separation Membranes Made from Co-Synthesized Nanoscale Cermet Powders.” *International Journal of Hydrogen Energy* 32:3631-3639.

Harvey SD and TJ Wenzel. 2008. “Selective Gas-Phase Capture of Explosives on Metal Beta-Diketonate Polymers.” *Journal of Chromatography A* 1192(2):212-217.

Havre SL, A Shah, C Posse, and BJM Webb-Robertson. 2006. “Diverse Information Integration and Visualization.” In *Visualization and Data Analysis 2006*, January 15-19, 2006, San Jose, California. *Proceedings of SPIE* vol. 6060, ed. RF Erbacher, JC Roberts, MT Gröhn, and K Börner. SPIE: The International Society for Optical Engineering, Bellingham, Washington.

Havre SL, BJM Webb-Robertson, A Shah, C Posse, B Gopalan, and FJ Brockman. 2005. “Bioinformatic Insights from Metagenomics Through Visualization.” In *Proceedings of the IEEE Computational Systems Bioinformatics Conference (CSB 2005)*. August 8-11, 2005, pp. 341-350. IEEE Computer Society, Los Alamitos, California.

Henager CH, Jr, AL Schemer-Kohrn, SG Pitman, DJ Senor, KJ Geelhood, and CL Painter. 2008. “Pitting Corrosion in CVD SiC at 300°C in Deoxygenated High-Purity Water.” *Journal of Nuclear Materials* 378 (1):9-16.

Hendricks TJ and NK Karri. 2007. “Design Impacts of Stochastically-Varying Input Parameters on Advanced Thermoelectric Conversion Systems.” In *26th International Conference on Thermoelectrics, ICT 2007*, pp. 343-352. IEEE, Piscataway, New Jersey.

Holbery J and D Houston. 2006. “Low-Cost Composites in Vehicle Manufacture – Natural-Fiber-Reinforced Polymer Composites in Automotive Applications.” *The Journal of the Minerals, Metals and Materials Society* 58(11):80-86.

Hook SE, AD Skillman, B Gopalan, JA Small, and IR Schultz. 2008. “Gene Expression Profiles in Rainbow Trout, *Onchorynchus mykiss*, Exposed to a Simple Chemical Mixture.” *Toxicological Sciences* 102(1):42-60.

Hu JZ, DN Rommereim, KR Minard, A Woodstock, BJ Harrer, RA Wind, RP Phipps, and PJ Sime. 2008. “Metabolomics in Lung Inflammation: A High Resolution ^{1}H NMR Study of Mice Exposed to Silica Dust.” *Toxicology Mechanisms and Methods* 18(5):385-398.

Huang Z and J Nieplocha. 2008. “Transforming Power Grid Operations via High Performance Computing.” In *IEEE Power Engineering Society General Meeting 2008*. IEEE, Piscataway, New Jersey.

Jaffe JE. 2007. “Energy and Length Scales in Scintillator Nonproportionality.” *Nuclear Instruments and Methods in Physics Research: Section A, Accelerators, Spectrometers, Detectors and Associated Equipment* 580(3):1378-1382.

Jarman KH, HW Kreuzer-Martin, DS Wunschel, NB Valentine, JB Cliff, CE Petersen, HA Colburn, and KL Wahl. 2008. “Bayesian Integrated Microbial Forensics.” *Applied and Environmental Microbiology* 74(11):3573-3582.

Josephson GB, JGH Geeting, DL Lessor, and WB Barton. 2006. “Axial Dispersion During Hanford Saltcake Washing.” In *14th Symposium on Separation Science and Technology for Energy Applications*, Gatlinburg, Tennessee, October 23-27, 2005. Published in *Separation Science and Technology* 41(10):2267-2282. Taylor & Francis Inc., Philadelphia, Pennsylvania.

Kerisit SN, KM Rosso, and BD Cannon. 2008. “Kinetic Monte Carlo Model of Scintillation Mechanisms in CsI and CsI(Tl).” *IEEE Transactions on Nuclear Science* 55(3 Pt. 2):1251-1258.

Lei C, Y Shin, JK Magnuson, GE Fryxell, LL Lasure, DC Elliott, J Liu, and EJ Ackerman. 2006. “Characterization of Functionalized Nanoporous Supports for Protein Confinement.” *Nanotechnology* 17(22):5531-5538.

Li G, D Hu, GG Xia, JM White, and ZC Zhang. 2008. “High Throughput Operando Studies Using Fourier Transform Infrared Imaging and Raman Spectroscopy.” *Review of Scientific Instruments* 79:074101.

Li XS, GE Fryxell, CM Wang, and MH Engelhard. 2008. “The Synthesis of Ag-Doped Mesoporous TiO_2.” *Microporous and Mesoporous Materials* 111(1-3):639-642.

Lin YY, J Wang, G Liu, H Wu, CM Wai, and Y Lin. 2008. “A Nanoparticle Label/Immunochromatographic Electrochemical Biosensor for Rapid and Sensitive Detection of Prostate-Specific Antigen.” *Biosensors and Bioelectronics* 23(11):1659-1665.

Liu G and Y Lin. 2007. “Electrochemical Quantification of Single Nucleotide Polymorphisms Using Nanoparticle Probes.” *Journal of the American Chemical Society* 129(34):10394-10401.

Majors PD, JS Mclean, and JC Scholten. 2008. “NMR Bioreactor Development for Live In-Situ Microbial Functional Analysis.” *Journal of Magnetic Resonance* 192(1):159-166.

Makarov YV, J Ma, N Zhou, CH Miller, TB Nguyen, and ED Tuglie. 2008. “A Cell Method Based on Pmu Measurements for Power System Dynamic Monitoring.” In *2008 International World Energy System Conference*. PNNL-SA-59736, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Matyas J, SK Sundaram, BJ Hicks, AB Edmondson, and BM Arrigoni. 2008. “Slag Refractory Interaction in Slagging Coal Gasifiers.” In *7th International Symposium on High-Temperature Corrosion and Protection of Materials*. Materials Science Forum.

Matyas J, SK Sundaram, CP Rodriguez, AB Edmondson, and BM Arrigoni. 2008. “Slag Penetration into Refractory Lining of Slagging Coal Gasifier.” In *Twenty-Fifth Annual International Pittsburgh Coal Conference 2008*. PNNL-SA-62047, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Mclean JS, PD Majors, CL Reardon, CL Bilskis, SB Reed, MF Romine, and JK Fredrickson. 2008. “Investigations of Structure and Metabolism within Shewanella oneidensis MR-1 Biofilms.” *Journal of Microbiological Methods* 74(1):47-56.

Mclean JS, GE Pinchuk, OV Geydebrekht, CL Bilskis, BA Zakrajsek, EA Hill, D Saffarini, MF Romine, YA Gorby, JK Fredrickson, and AS Beliaev. 2008. “Oxygen-Dependent Autoaggregation in Shewanella oneidensis MR-1.” *Environmental Microbiology* 10(7):1861-1876.

Mei D, NA Deskins, M Dupuis, and Q Ge. 2008. “Density Functional Theory Study of Methanol Decomposition on the CeO2(110) Surface.” *Journal of Physical Chemistry C* 112(11):4257-4266.

Metz TO, JS Page, ES Baker, K Tang, J Ding, Y Shen, and RD Smith. 2008. “High Resolution Separations and Improved Ion Production and Transmission in Metabolomics.” *Trends in Analytical Chemistry. TrAC* 27(3):205-214.

Miracle AL, VL Bailey, SE Baker, AL Bunn, JK Magnuson, and BJM Webb-Robertson. 2007. “Integration of ’Omics Technologies for Characterization of Complex Microbial Ecosystems.” In *Waste Management Symposium 2008*, pp. 832-841.

Nieplocha J, A Marquez, V Tipparaju, D Chavarría-Miranda, RT Guttromson, and Z Huang. 2006. “Towards Efficient Parallel State Estimation Solvers on Shared Memory Computers.” In *Highspeed Computation Panel of the Proceedings of the 2006 IEEE Power Engineering Society General Meeting*, June 18-22, 2006, pp. 1-5. IEEE, Piscataway, New Jersey.

Olsen LC, ME Gross, SN Kundu, and GL Graff. 2008. “Properties of Encapsulated CIGS Cells in 85C/85%RH.” In *The 31st IEEE Photovoltaic Specialists Conference*. PNNL-SA-60866, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Palmer BJ, SM Kathmann, MK Krishnan, V Tipparaju, and J Nieplocha. 2007. “The Use of Processor Groups in Molecular Dynamics Simulations to Sample Free-Energy States.” *Journal of Chemical Theory and Computation* 3(2):583-592.

Peper SM, BK McNamara, MJ O’Hara, and M Douglas. 2008. “A Green Approach to SNF Reprocessing: Are Common Household Reagents the Answer?” In *8th International Conference on Facility Operations-Safeguards Interface*, Portland, Oregon, March 30-April 4, 2008.

Pike WA, C Scherrer, and SJ Zabriskie. 2008. “Putting Security in Context: Visual Correlation of Network Activity with Real-World Information.” In *VizSEC 2007: Proceedings of the Workshop on Visualization for Computer Security*, ed. JR Goodall, G Conti, and KL Ma, pp. 203-220. Springer, Berlin, Germany.

Polpitiya AD, W Qian, N Jaitly, VA Petyuk, JN Adkins, DG Camp, II, GA Anderson, and RD Smith. 2008. “DAnTE: A Statistical Tool for Quantitative Analysis of –Omics Data.” *Bioinformatics* 24(13):1556-1558.

Posse C, AP Sanfilippo, B Gopalan, RM Riensche, N Beagley, and BL Baddeley. 2006. “Cross-Ontological Analytics: Combining Associative and Hierarchical Relations in the Gene Ontologies to Assess Gene Product Similarity.” In *Computational Science – ICCS 2006: 6th International Conference*, Reading, United Kingdom, May 28-31, 2006. Proceedings, Part II : 2006 International Workshop on Bioinformatics Research and Applications, IWBRA’06, Vol. 3992, ed. VN Alexandrov, GD van Albada, PMA Sloot, and J Dongarra, pp. 871-878. Springer, Berlin/Heidelberg, Germany.

Qian W and DJ Bigelow. 2008. “Quantitative Proteome Mapping of Nitrotyrosines.” In *Methods in Enzymology, Nitric Oxide Part F: Oxidative and Nitrosative Stress in Redox Regulation of Cell Signaling*, Vol. 440, pp. 191-205. Elsevier, Amsterdam, Netherlands.

Sanfilippo AP, C Posse, B Gopalan, SC Tratz, and ML Gregory. 2006. “Integrating Ontological Knowledge and Textual Evidence in Estimating Gene and Gene Product Similarity.” In *Human Language Technology Conference/North American Chapter of the Association for Computational Linguistics Annual Meeting (HLT-NAACL)*, June 8-9, 2006, New York City, New York. Proceedings of the BioNLP’06 Workshop on Linking Natural Language Processing and Biology: Towards Deeper Biological Literature Analysis, pp. 25-32. The Association for Computational Linguistics, East Stroudsburg, Pennsylvania.

Saripalli P, JE Amonette, FC Rutz, and N Gupta. 2006. “Design of Sensor Networks for the Long Term Monitoring of Geological Sequestration.” *Energy Conversion and Management* 47(13-14):1968-1974.

Shah AR, CS Oehmen, and BJM Webb-Robertson. 2008. “SVM-Hustle – An Iterative Semi-Supervised Machine Learning Approach for Pairwise Protein Remote Homology Detection.” *Bioinformatics* 24(6):783-790.

Shankaran H, Y Zhang, L Opresko, and H Resat. 2008. “Quantifying the Effects of Co-Expressing EGFR and HER2 on HER Activation and Trafficking.” *Biochemical and Biophysical Research Communications* 371(2):220-224.

Shaw WJ, Y Chen, JL Fulton, JC Linehan, A Gutowska, and TE Bitterwolf. 2008. “Structural Evolution of a Recoverable Rhodium Hydrogenation Catalyst.” *Journal of Organometallic Chemistry* 693(12):2111-2118.

Shi L, S Deng, MJ Marshall, Z Wang, DW Kennedy, A Dohnalkova, HM Mottaz, EA Hill, YA Gorby, AS Beliaev, DJ Richardson, JM Zachara, and JK Fredrickson. 2008. “Direct Involvement of Type II Secretion System in Extracellular Translocation of Shewanella Oneidensis Outer Membrane Cytochromes MtrC and OmcA.” *Journal of Bacteriology* 190(15):5512-5516.

Shin Y, GE Fryxell, C Johnson, and MM Haley. 2008. “Templated Synthesis of Pyridine Functionalized Mesoporous Carbons Through the Cyclotrimerization of Diethynylpyridines.” *Chemistry of Materials* 20(3):981-986.

Shvartsburg AA and RD Smith. 2008. “Optimum Waveforms for Differential Ion Mobility Spectrometry (FAIMS).” *Journal of the American Society for Mass Spectrometry* 19(9):1286-1295.

Straub TM, RA Bartholomew, CO Valdez, CJ Bruckner-Lea, A Dohnalkova, K Honer, Z Bentrup, CP Gerba, P Orosz Coghlan, C Nickerson, Ph.D., M Abbaszadegan, and B Mayer. 2006. “Human Norovirus Infection of Differentiated Human Small Intestinal Cells.” *Nature*.

Sundaram SK and TJ Weber. 2008. “Special Issue on Nanotoxicity.” *International Journal of Nanotechnology*. [In press]

Talbott TD, KL Schuchardt, EG Stephan, and JD Myers. 2006. “Mapping Physical Formats to Logical Models to Extract Data and Metadata: The Defuddle Parsing Engine.” In *IPAW’06: International Provenance and Annotation Workshop*, Chicago, Illinois, May 3-5, 2006. Lecture Notes in Computer Science, vol. 4145, ed. L Moreau and I Foster, pp. 73-81. Springer-Verlag, Berlin, Germany.

Tartakovsky AM, GD Redden, PC Lichtner, TD Scheibe, and P Meakin. 2008. “Mixing-Induced Precipitation: Experimental Study and Multi-Scale Numerical Analysis.” *Water Resources Research* 44(6):Art. No. W06S04.

Taylor RC, G Acquaah-Mensah, M Singhal, D Malhotra, and S Biswal. 2008. “Network Inference Algorithms Elucidate Nrf2 Regulation of Mouse Lung Oxidative Stress.” *PLoS Computational Biology* 4(8):Art. No. e1000166.

Taylor RC, M Singhal, DS Daly, JM Gilmore, KO Domico, AM White, DL Auberry, KJ Auberry, BS Hooker, GB Hurst, JE McDermott, WH McDonald, DA Pelletier, DA Schmoyer, and WR Cannon. 2008. “An Analysis Pipeline for the Inference of Protein-Protein Interaction Networks.” *International Journal of Data Mining and Bioinformatics*. [In press]

Taylor RC, M Singhal, JB Weller, S Khoshnevis, L Shi, and JE McDermott. 2008. “A Network Inference Workflow Reveals Functional Groups, Metabolic Pathways, and Regulons in Salmonella typhimurium.” In *Annals of the New York Academy of Sciences*. [In press]

Teeguarden JG, A Gupta, P Escobar, and M Jackson. 2008. “Toxicology Steps Up to Nanotechnology Safety.” *Research & Development* 50(1):28-29.

Thallapally PK, BP McGrail, SJ Dalgarno, and JL Atwood. 2008. “Gas/Solvent-Induced Transformation and Expansion of a Nonporous Solid to 1:1 Host Guest Form.” *Crystal Growth & Design* 8(7):2090-2092.

Thallapally PK, BP McGrail, SJ Dalgarno, HT Schaef, J Tian, and JL Atwood. 2008. “Gas-Induced Transformation and Expansion of a Non-Porous Organic Solid.” *Nature Materials* 7(2):146-150.

Thurman DA, JP Almquist, I Gorton, AS Wynne, and J Chatterton. 2007. “SIFT – A Component-Based Integration Architecture for Enterprise Analytics.” In *ICCBSS ’07: Sixth International IEEE Conference on Commercial-off-the-Shelf (COTS)-Based Software Systems*, February 26-March 2, 2007, Banff, Alberta, Canada, pp. 82-92. Institute of Electrical and Electronics Engineers, Piscataway, New Jersey.

Towne SA, VV Viswanathan, J Holbery, and PC Rieke. 2007. “Fabrication of Polymer Electrolyte Membrane Fuel Cell MEAs Utilizing Inkjet Print Technology.” *Journal of Power Sources* 171(2):575-584.

Wang D, D Choi, Z Yang, VV Viswanathan, Z Nie, CM Wang, Y Song, J Zhang, and J Liu. 2008. “Synthesis and Li-ion Insertion Properties of Highly Crystalline Mesoporous Rutile TiO_2.” *Chemistry of Materials* 20(10):3435-3442.

Wang D, Z Ma, S Dai, J Liu, Z Nie, MH Engelhard, Q Huo, CM Wang, and R Kou. 2008. "Low-Temperature Synthesis of Tunable Mesoporous Crystalline Transition Metal Oxides and Applications as Au Catalyst Supports." *Journal of Physical Chemistry C* 112(35):13499-13509.

Wang J, G Liu, and Y Lin. 2008. "Layer-by-Layer Assembly of Enzymes on Carbon Nanotubes." Chapter 6 in *Biomolecular Catalysis Nanoscale Science and Technology, ACS Symposium Series* 986, ed. J Kim, SH Kim, and P Wang, pp. 117-128. American Chemical Society, Washington, District of Columbia.

Wang LQ, D Wang, J Liu, GJ Exarhos, S Pawsey, and IL Moudrakovski. 2009. "Probing Porosity and Pore Interconnectivity in Crystalline Mesoporous TiO_2 Using Hyperpolarized 129Xe NMR." *Journal of Physical Chemistry*. [In press]

Wang P and J Laskin. 2008. "Helical Peptide Arrays on Self-Assembled Monolayer Surfaces Through Soft and Reactive Landing of Mass-Selected Ions." *Angewandte Chemie International Edition* 47:6678-6680.

Wang Z, C Liu, X Wang, MJ Marshall, JM Zachara, KM Rosso, M Dupuis, JK Fredrickson, SM Heald, and L Shi. 2008. "Kinetics of Reduction of Fe(III) Complexes by Outer Membrane Cytochromes MtrC and OmcA of Shewanella oneidensis MR-1." *Applied and Environmental Microbiology* 74(21):6746-6755.

Waters KM, LM Masiello, RC Zangar, BJ Tarasevich, NJ Karin, RD Quesenberry, S Bandyopadhyay, JG Teeguarden, JG Pounds, and BD Thrall. 2009. "Macrophage Responses to Silica Nanoparticles are Highly Conserved Across Particle Sizes." *Toxicological Sciences* 107(2):553-569.

Webb-Robertson BJM, WR Cannon, CS Oehmen, AR Shah, V Gurumoorthi, MS Lipton, and KM Waters. 2008. "A Support Vector Machine Model for the Prediction of Proteotypic Peptides for Accurate Mass and Time Proteomics." *Bioinformatics* 24(13):1503-1509.

Webb-Robertson BJM, KF Ferris, and DM Jones. 2008. "Design Rules for Ce-Activated Scintillating Radiation Detection Materials: Compromises Between Luminosity and Stopping Power." *IEEE Transactions on Nuclear Science* 55(3:2):1210-1215.

Webb-Robertson BJM, LA McCue, and CE Lawrence. 2008. "Measuring Global Credibility with Application to Local Sequence Alignment." *PLoS Computational Biology* 4(5):Art. No. e1000077.

Wind RA, HC Bertram, and JZ Hu. 2005. "Slow-MAS NMR Methods to Study Metabolic Processes In Vivo and In Vitro." In *Magnetic Resonance in Food Science: The Multivariate Challenge*, ed. PS Belton, SB Engelsen, and HJ Jakobsen, pp. 156-165. Royal Society of Chemistry, New York, New York.

Wu H, MH Engelhard, J Wang, DR Fisher, and Y Lin. 2008. "Synthesis of Lutetium Phosphate/Apoferritin Core-Shell Nanoparticles for Potential Applications in Radioimmunoimaging and Radioimmunotherapy of Cancers." *Journal of Materials Chemistry* 18(15):1779-1783.

Wu H, Q Huo, SM Varnum, G Liu, J Wang, Z Nie, J Liu, and Y Lin. 2008. "Dye-Doped Silica Nanoparticle Labels/Protein Microarray for Detection of Protein Biomarkers." *The Analyst* 133:1550-1555.

Wu H, J Wang, Z Wang, DR Fisher, and Y Lin. 2008. "Apoferritin-Templated Yttrium Phosphate Nanoparticle Conjugates for Radioimmunotherapy of Cancers." *Journal of Nanoscience and Nanotechnology* 8(5):2316-2322.

Wunschel DS, JH Wahl, AR Willse, KH Jarman, JA Small, CE Petersen, NB Valentine, and KL Wahl. 2008. "MALDI-MS and Capillary HPLC-MALDI-MS of Small Protein Markers: Applications in Microbial Identification, Forensics and Host Response Assessment." In *Tenth International Symposium on Hyphenated Techniques in Chromatography and Hyphenated Chromatographic Analyzers & Tenth International Symposium on Advances in Extraction Techniques 2008 & Public Safety and Security – The Hyphenated Chromatographic Approach*. HTC Meeting, Brugge, Belgium.

Wynne AS, I Gorton, JP Almquist, J Chatterton, and DA Thurman. 2008. "A Flexible, High Performance Service-Oriented Architecture for Detecting Cyber Attacks." In *Proceedings of the 41st Annual Hawaii International Conference on System Sciences*, p. 263. IEEE Computer Society, Los Alamitos, California.

Zangar RC, N Bollinger, S Verma, NJ Karin, and Y Lu. 2008. "The Nuclear Factor-kB Pathway Regulates Cytochrome P450 3A4 Protein Stability." *Molecular Pharmacology* 73(6):1652-1658.

Zhang Y, M Elfman, BD Milbrath, and WJ Weber. 2008. "Evaluate Scintillation Response Over a Continuous Energy Region." *IEEE Transactions on Nuclear Science* 55(3):1097-1101.

Zhang Y, X Xiang, and WJ Weber. 2008. “Scintillation Response of CaF_2 to H and He over a Continuous Energy Range.” *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* 266(12-13):2750-2753.

Zhong L, M Oostrom, TW Wietsma, and MA Covert. 2008. “Enhanced Remedial Amendment Delivery through Fluid Viscosity Modifications: Experiments and Numerical Simulations.” *Journal of Contaminant Hydrology* 101(1-4):29-41.

Ziegler SL and BA Bushaw. 2008. “Ultratrace Uranium Fingerprinting with Isotope Selective Laser Ionization Spectrometry.” *Analytical Chemistry* 80(15):6029-6033.

Appendix B

Fiscal Year 2008 Non-Refereed Publications

Appendix B
Fiscal Year 2008 Non-Refereed Publications

In this appendix, 127 non-refereed publications or presentations resulting from PNNL's LDRD Program during FY 2008 are arranged in alphabetical order by the first author's last name.

2008. PNWD-3927 [Limited Distribution]

2008. PNWD-SA-8135 [Limited Distribution]

Alexander ML, HW Kreuzer, M Newburn, and A Mendoza. 2008. "Applications of On-Line Aerosol Mass Spectrometry Outside of Atmospheric Science." Presented by Liz Alexander at the 2nd On-Line Particle Mass Spectrometry Workshop, Leeds, United Kingdom, April 9, 2008 (invited).

Atkinson DA. 2008. "Explosives Detection Research at PNNL: The Chemistry Approach." Presented by David Atkinson at the Gonzaga University Collaboration Meetings, Spokane, Washington, February 29, 2008.

Baker ES, AM Mayampurath, N Jaitly, BH Clowers, R Zhao, K Tang, EA Livesay, DJ Orton, B Danielson, III, ME Belov, and RD Smith. 2008. "Characterization and Use of Drift Times from Features in LC-IMS-MS Experiments." Presented by Erin S. Baker at the American Society for Mass Spectrometry, Denver, Colorado, June 2, 2008 (invited).

Bandyopadhyay S, LM Masiello, NJ Karin, BJM Webb-Robertson, JM Jacobs, JG Pounds, BD Thrall, and KM Waters. 2008. "Integration of Microarray and Proteomic Data Reveals Pathway-Specific Inflammatory Markers of Nanoparticle Exposure to Mouse Macrophages." Presented by Katrina Waters at the Society of Toxicology Annual Meeting, Seattle, Washington, March 17, 2008.

Bapanapalli SK and BN Nguyen. 2008. "Forming Prediction of Magnesium Alloy Sheets Using a Continuum Damage Mechanics Multistep Inverse Approach." In Proceedings of ASME 2008 International Mechanical Engineering Congress and Exposition. ASME International Mechanical Engineering Congress and Exposition, Boston, Massachusetts.

Beagley N, C Posse, AM White, and PD Whitney. 2008. "Anomaly Detection in Internet Traffic Data." Presented by Nathaniel Beagley at JSM 2008, Denver, Colorado, August 3, 2008 (invited).

Bernacki BE and N Ho. 2008. "Differential Spectroscopic Imaging of Particulate Explosives Residue." In Proceedings of the SPIE: Optics and Photonics in Global Homeland Security IV, Vol. 6945, eds. CS Halvorson, D Lehrfeld, and TT Saito, Art. No. 694517. SPIE, Bellingham, Washington.

Buchko GW, H Robinson, CY Rolston, A Addlagatta, and DW Koppenaal. 2008. "Structural Characterization of Two Proteins in the DUF683 and DUF269 Families Associated with Nitrogen Fixation in the Cyanbacterium Cyanothece 51142." Presented by Garry W. Buchko at the Northwest Crystallography Workshop, Eugene, Oregon, June 20, 2008.

Campbell LW, F Gao, R Devanathan, and WJ Weber. 2006. "Model of Plasmon Decay for Electron Cascade Simulation." Presented by Luke Campbell at the 2006 Symposium on Radiation Measurements and Applications, Ann Arbor, Michigan, May 23, 2006.

Chase JM, KL Schuchardt, G Chin, Jr, JA Daily, and TD Scheibe. 2008. "Iterative Workflows for Numerical Simulations in Subsurface Sciences." Presented by Jared M. Chase at the IEEE 2008 Services Conference, Honolulu, Hawaii, July 10, 2008.

Cheng L, Q Ge, and D Mei. 2008. "Effects of Zr Dopant on Vacancy Formation in Ceria: A Density Functional Theory Study." Presented by Lei Cheng at the ACS 2008 Spring Meeting, New Orleans, Louisiana, April 18, 2008.

Cziczo DJ. 2008. "The Chemical Composition of Ice Nuclei in Ice and Mixed-Phase Clouds: Studies at a High Altitude Research Station in Switzerland." Presented by Dan Cziczo at the 2008 Joint Assembly, Fort Lauderdale, Florida, May 28, 2008.

Cziczo DJ, H Herich, L Keller, SJ Gallavardin, and U Lohmann. 2008. "Which Aerosol Particles End Up Inside Clouds?" Presented by Dan Czizco at the AGU Joint Assembly Meeting, Fort Lauderdale, Florida, May 29, 2008.

Douglas M, SM Peper, BK McNamara, and MJ O'Hara. 2008. "Dissolution of Uranium Oxide in Oxidizing Alkaline Solutions." Presented by Matt Douglas at the 32nd Annual Actinide Separations Conference, Park City, Utah, May 13, 2008.

DuBois DL. 2008. “An Energy-Based Approach to the Development of Hydrogen Oxidation/Production, Hydrogen Storage, and Carbon Dioxide Reduction Catalysts.” Presented by Daniel L. DuBois at the MRS International Materials Research Conference, Chongqing, China, June 10, 2008 (invited).

Duckworth DC, M Douglas, SM Peper, OT Farmer, III, SA Lehn, M Liezers, and JM Schwantes. 2008. “A Novel Approach to Near Real Time Non-Destructive Analysis of Pu for Process Monitoring and Material Safeguards.” Presented by Douglas C. Duckworth at the Institute of Nuclear Materials Management 49th Annual Meeting, Nashville, Tennessee, July 16, 2008.

Duckworth DC, SA Lehn, and M Liezers. 2008. “Electrochemically-Modulated Separation and Mass Spectrometric Analysis of Actinides in Difficult Matrices.” Presented by Douglas C. Duckworth at the Institute of Nuclear Materials Management’s 8th International Conference on Facilities Ops-Safeguards Interface, Portland, Oregon, April 1, 2008.

Duckworth DC, M Liezers, SA Lehn, and M Douglas. 2008. “Electrochemically-Modulated Separation and Mass Spectrometric Analysis of Actinides in Difficult Matrices.” Presented by Doug C. Duckworth, Martin Liezers, Scott A. Lehn, and Matt Douglas at the INMM 8th International Conference on Facility Operations-Safeguards Interface, Portland, Oregon, April 1, 2008.

Dyedov V, DR Einstein, J Xiangmin, AP Kuprat, and F del Pin. 2008. “Scale-Invariant Boundary-Layer Mesh Generation Using Face Offsetting for Biomedical Computing.” In the 17th International Meshing Roundtable. PNWD-SA-8233, Battelle-Pacific Northwest Division, Richland, Washington. [Unpublished]

Ewing RG and MJ Waltman. 2008. “Negative Ionization Chemistry Occurring in Discharge Sources.” Presented by Robert Ewing at the 17th International Conference on Ion Mobility Spectrometry, Ottawa, Ontario, Canada, July 21, 2008.

Ewing RG, MJ Waltman, and DA Atkinson. 2007. “A Study on the Fragmentation of Explosive Adducts with Cl-, NO_3- and CO_3-Reactant Ions.” Presented by Robert Ewing at the 16th International Conference on Ion Mobility Spectrometry, Mikkeli, Finland, July 25, 2007.

Fan J, M Ovtchinnikov, JM Comstock, SA McFarlane, and A Khain. 2008. “Modeling Arctic Mixed-Phase Clouds and Associated Ice Formation.” Presented by Jiwen Fan at the International Commission on Clouds and Precipitation, Cancun, Mexico, July 8, 2008.

Farber RM. 2008. “Back to the Future: The Return of Massively Parallel Systems.” Scientific Computing: Information Technology for Science Online. http://www.scientificcomputing.com/Back_to_the_Future.aspx?terms=back%20to%20the%20future.

Farber RM and HE Trease. 2008. “Massively Parallel Near-Linear Scalability Algorithms with Application to Unstructured Video Analysis.” In TeraGrid ’08. PNNL-SA-59990, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Farber RM and HE Trease. 2008. “Massively Parallel Near-Linear Scalability Algorithms with Application to Unstructured Video Analysis.” Presented by Rob Farber at TeraGrid ’08, Las Vegas, Nevada, June 10, 2008 (invited).

Farber RM, HE Trease, and ST Elbert. 2008. “General Massively Parallel Near-Linear Scalability Algorithms and Application to Generate Searchable Information.” In TeraGrid ’08. PNNL-SA-60093, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Fast JD, WI Gustafson Jr, EG Chapman, DJ Baxter, GA Grell, and M Barth. 2008. “Update on the Development of the Aerosol Modeling Testbed.” Presented by Jerome D. Fast at the 9th WRF Users’ Workshop, Boulder, Washington, June 23, 2008.

Fast JD, WI Gustafson Jr, EG Chapman, DJ Baxter, JP Rishel, G Grell, and M Barth. 2008. “The Aerosol Modeling Testbed: A Proposed Tool to Facilitate Improved Aerosol Process Modules.” Presented by Jerome D. Fast at the 2008 Atmospheric Science Program (ASP) Science Team Meeting, Annapolis, Maryland, February 25, 2008.

Felix EJ and J Nieplocha. 2006. “Advanced Data Processing with Active Storage.” Presented by Evan Felix at Supercomputing 2006, Tampa, Florida, November 14, 2006.

Ferris KF and BJM Webb-Robertson. 2008. “Materials Discovery: Accelerating Identification and Development through Informatics.” Presented by Kim F. Ferris at the NA-22 Materials Discovery Briefing, July 16, 2008 (invited).

Ferris KF, BJM Webb-Robertson, and DM Jones. 2008. “Knowledge-Based Estimation of Electronic Properties in Ternary Materials.” Presented by Kim F. Ferris at SORMA 2008, Berkeley, California, June 2, 2008.

Ferris KF, BJM Webb-Robertson, and DM Jones. 2008. “Virtual Candidate Spaces: Developing Design Rules for Data-Driven Exploration.” Presented by Kim F. Ferris at the TMS 2008 Annual Meeting, New Orleans, Louisiana, March 12, 2008 (invited).

Ferris KF, BJM Webb-Robertson, DM Jones, and A Heredia-Langner. 2008. “Accelerating Materials Discovery: Developing Design Rules for Data-Driven Exploration.” Presented by Kim F. Ferris at the Sanibel Symposium, St. Simons Island, Georgia, February 23, 2008 (invited).

Ferryman TA. 2008. “Program Status Statistical Analysis of Abnormal Behavior.” Presented by Thomas A. Ferryman at DOE/CERTS, TVA, and SOC Review, May 27, 2008 (invited).

Ferryman TA and BG Amidan. 2008. “Statistical Analysis of PMU Data.” Presented by Thomas A. Ferryman at DOE/CERTS, TVA, and SOC Review, May 29, 2008 (invited).

Ferryman TA and BG Amidan. 2008. “Statistical Analysis of PMU Data – Program Status – Closing Remarks.” Presented by Thomas A. Ferryman at DOE/CERT, TVA, and SOC Review, May 29, 2008 (invited).

Ferryman TA and BG Amidan. 2008. “Statistical Analysis of PMU Data – Program Status – Derived Variables.” Presented by Thomas A. Ferryman at DOE/CERT, TVA, and SOC Review, May 29, 2008 (invited).

Ferryman TA and BG Amidan. 2008. “Statistical Analysis of PMU Data – Program Status – Derived Variables: Comparison of Pairs of VH Data within Same Organization.” Presented by Thomas A. Ferryman at DOE/CERT, TVA, and SOC Review, May 29, 2008 (invited).

Ferryman TA and BG Amidan. 2008. “Statistical Analysis of PMU Data – Program Status – Displays and Drilldowns.” Presented by Thomas A. Ferryman at DOE/CERT, TVA, and SOC Review, May 29, 2008 (invited).

Ferryman TA and BG Amidan. 2008. “Statistical Analysis of PMU Data – Program Status – Power Grid Monitoring and Alerting System (Morning Report) Statistical Analysis Tool to Identify Atypical Events and Pre-Cursors.” Presented by Thomas A. Ferryman at DOE/CERT, TVA, and SOC Review, May 29, 2008 (invited).

Ferryman TA, BG Amidan, and SK Cooley. 2008. “Statistical Analysis of PMU Data – Program Status.” Presented by Thomas A Ferryman at DOE/CERT, TVA, and SOC Review, May 29, 2008 (invited).

Fink GA. 2007. “Who’s the Boss? Autonomics and New-Fangled Security Gizmos with Minds of Their Own: An Invited Talk for USENIX LISA 2007.” Presented by Glenn Fink at USENIX LISA 2007, Dallas, Texas, November 14, 2007 (invited).

Fink GA, NC Rowe, and D Grosu. 2008. “Active Deception for Military Operational Computers.” Presented by Glenn Fink at the Phoenix Challenge Conference, Spring 2008, San Antonio, Texas, April 2, 2008.

Gao F, YL Xie, LW Campbell, AJ Peurrung, and WJ Weber. 2008. “Intrinsic Properties and Nanostructure of Electron-Hole Distribution in CsI and CdZnTe.” Presented by Fei Gao at the 2008 Symposium on Radiation Measurements and Applications, Berkeley, California, June 4, 2008.

Gaspar DJ, AL Miracle, AL Bunn, JA Ward, JM Brandenberger, JG Teeguarden, BJ Tarasevich, and JG Pounds. 2008. “A Systems Approach to Understanding the Potential for Environmental Effects Resulting from the Production and Use of Engineered Nanomaterials.” Presented by Daniel J. Gaspar at NanoECO – Nanoparticles in the Environment – Implications and Applications, Monte Verita, Switzerland, March 4, 2008.

Gibson TD and EG Stephan. 2008. “Application of Provenance for Automated and Research Driven Workflows.” Presented by Tara Gibson at the Second International Provenance and Annotation Workshop, Salt Lake City, Utah, June 17, 2008.

Gill K, MS Wigmosta, A Coleman, R Prasad, and LW Vail. 2007. “Ensemble Streamflow Forecasting via Data Assimilation.” Presented by M. Kashif Gill at the American Geophysical Union, Fall 2007, San Francisco, California, December 13, 2007.

Good MS, PC Durst, JR Skorpik, and DW Wootan. 2008. “An Unattended and Secure Monitor Concept for Spent Nuclear Fuel Containers.” Presented by Morris S. Good at the Institute of Nuclear Materials Management 49th Annual Meeting, Nashville, Tennessee, July 17, 2008.

Greitzer FL. 2008. “A Sensemaking Perspective on Situation Awareness in Power Grid Operations.” Presented by Frank L. Greitzer at the IEEE Power Engineering Society General Meeting, Pittsburgh, Pennsylvania, July 21, 2008 (invited).

Greitzer FL and DH Andrews. 2008. “Training Strategies to Mitigate Expectancy-Induced Response Bias in Combat Identification: A Research Agenda [Keynote Address].” Presented by Frank L. Greitzer and Dee H. Andrews at the Human Factors in Combat Identification Workshop, Mesa, Arizona, May 13, 2008 (invited).

Heibeck TH, SJ Ding, L Opresko, R Zhao, AA Schepmoes, ME Monroe, DG Camp, II, RD Smith, HS Wiley, and W Qian. 2008. "Quantitative Analysis of Receptor Tyrosine Signaling in Stimulated Human Mammary Epithelial Cells." Presented by Tyler Heibeck at the 56th ASMS Conference on Mass Spectrometry and Allied Topics, Denver, Colorado, June 2, 2008.

Hendricks TJ. 2008. "Robust Design of Advanced Thermoelectric Conversion Systems: Probabilistic Design Impacts on Specific Power and Power Flux Optimization." Presented by Terry J. Hendricks at the 2008 MRS Spring Meeting, San Francisco, California, March 24, 2008 (invited).

Hendricks TJ and NK Karri. 2008. "Robust Design of Advanced Thermoelectric Conversion Systems: Probabilistic Design Impacts on Specific Power and Power Flux Optimization." In MRS Spring 2008. PNNL-SA-59804, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Heredia-Langner A, KF Ferris, X Sun, and PD Whitney. 2008. "Inverse Mapping Structures onto Transparency." Presented by Alejandro Heredia-Langner at the American Physical Society, New Orleans, Louisiana, March 12, 2008.

Hoyt DW, NG Isern, SD Burton, JJ Ford, MJ Froehlke, HM Cho, JZ Hu, AS Lipton, and PD Ellis. 2008. "Unique Capabilities at a User Facility to Support the Study of Biosystems/Materials in Solid- and Liquid-State Spectroscopy." Presented by David Hoyt at the 49th ENC Conference, Pacific Grove, California, March 10, 2008.

Hu D, AB Padmaperuma, X Cai, HA Qiao, and PE Burrows. 2008. "STM Luminescence Imaging of Organic Light Emitting Devices." Presented by Dehong Hu at the Joint Northwest & Rocky Mountain Regional Meeting of the American Chemical Society, Park City, Utah, June 16, 2008.

Hu JZ, Q Zhang, DN Rommereim, NG Isern, DW Hoyt, TO Metz, and K Mcateer. 2008. "Metabolic Changes in Mice Exposed to High Let Iron Ion and Proton Radiation." Presented by Jianxhi Hu at the 19th Annual NASA Space Radiation Investigators Workshop, Philadelphia, Pennsylvania, June 30, 2008 (invited).

Huang Z and J Nieplocha. 2008. "Transforming Power Grid Operations via High Performance Computing." Presented by Zhenyu Huang at the IEEE Power and Energy Society General Meeting 2008, Pittsburgh, Pennsylvania, July 22, 2008 (invited).

Jacobs JM, W Qian, DJ Bigelow, CA Sacksteder, RA Corley, and RD Smith. 2008. "Characterization of Inflammatory/Oxidative Stress Protein Modifications." Presented by Jon Jacobs at the Human Proteome Organization Annual World Congress, Amsterdam, Netherlands, August 17, 2008.

Kim JY, KS Weil, JF Bonnett, Y Shin, and DJ Gaspar. 2008. "Non-Precious Metal Based Catalysts for PEM Fuel Cells." Presented by K. Scott Weil at the 2008 TMS Annual Meeting, New Orleans, Louisiana, March 12, 2008 (invited).

King DL, L Li, J Liu, Q Huo, and Y Wang. 2008. "Trapping Metal Nanoparticles in Cubic Mesostructures for Highly Efficient and Regenerable Deep Desulfurization of Warm Coal Gas." Presented by David L. King at the 14th International Catalysis Conference, Seoul, Korea, Democratic People's Republic of Korea, July 14, 2008.

Kottman RM, DN Rommereim, NG Isern, DW Hoyt, BJM Webb-Robertson, and JZ Hu. 2008. "Metabolomic Analysis Identifies Novel Pathways Dysregulated in Mouse and Human Pulmonary Fibrosis." Presented by RM Kottman at the International Fibrosis Colloquium Conference, Charlotte, North Carolina, June 10, 2008.

Li L, DL King, J Liu, K Zhu, Q Huo, and Y Wang. 2008. "Trapping Nickel Nanoparticles in Mesostructures for Regenerable Deep Desulfurization of Warm Syngases." Presented by Liyu Li at the 33rd International Technical Conference on Coal Utilization & Fuel Systems – "The Clearwater Coal Conference," Clearwater, Florida, June 4, 2008.

Liu W. 2008. "Micro-Channel Membranes for Advanced Separation and Reaction Technologies." Presented by Wei Liu at the 2008 Micro Nano Breakthrough Conference, Vancouver, Washington, September 8, 2008.

Liu W. 2008. "Molecular Separation Mechanisms and Industrial Applications of MFI-Type Zeolite Membranes." Presented by Wei Liu at the International Congress on Membranes and Processes, Honolulu, Hawaii, July 12, 2008.

Liu W, DC Elliott, Y Wang, BR Johnson, XS Li, and F Zheng. 2008. "Micro-Structured Inorganic Membrane Reactor." Presented by Wei Liu at the International Congress on Membranes and Processes, Honolulu, Hawaii, July 12, 2008.

Liu W, DL King, J Liu, Y Wang, BD Johns, and ZG Yang. 2007. "Critical Material and Process Issues for CO_2 Separation from Coal-Powered Plants." In TMS Symposium – Materials in Clean Power Systems III: Fuel Cells, Hydrogen-, and Clean Coal-Based Technologies. PNNL-SA-58412, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Liu W, D Wang, AJ Karkamkar, F Zheng, DL King, BR Johnson, and J Liu. 2008. "Novel Zeolite Adsorption Technology for CO_2 Capture." Presented by Wei Liu at the 33rd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, June 1, 2008.

Lumetta GJ, JM Billing, SA Bryan, BD Hanson, and TG Levitskaia. 2008. "Integration of Counter-Current Solvent Extraction Testing Capability with New Online Monitoring Tools." Presented by Gregg Lumetta at the 32nd Actinide Separations Conference, Park City, Utah, May 15, 2008.

Majors PD. 2008. "Live Microbial Physiology Studies Employing Nuclear Magnetic Resonance – The 'Swiss Army Knife' of Analytical Techniques." Presented by Paul D. Majors at the Chemical Engineering Department, Washington State University, Pullman, Washington, March 31, 2008 (invited).

Malone EL. 2008. "Resilience, Climate Change, and Security: Modeling the Connections." Presented by Elizabeth L. Malone at RESILIENCE 2008 – Resilience, Adaptation and Transformation in Turbulent Times/International Science and Policy Conference, Stockholm, Sweden, April 14, 2008.

McDermott JE, RC Taylor, L Shi, JN Adkins, and CK Ansong. 2008. "Modeling the Salmonella-Macrophage Host-Pathogen Interaction." Presented by Jason McDermott at the UW/NIDA Systems Biology Symposium, Seattle, Washington, June 30, 2008 (invited).

McDermott JE, RC Taylor, L Shi, JN Adkins, and CK Ansong. 2008. "Systems Biology of the Salmonella Host-Pathogen Interaction." Presented by Jason McDermott at the OHSU Microbiology Departmental Seminar Series, Portland, Oregon, May 27, 2008 (invited).

McFarlane SA, JM Comstock, J Fan, X Liu, M Ovtchinnikov, W Wang, Y Wang, and S Xie. 2008. "Remote Sensing Observations and Modeling for TWP-ICE." Presented by Sally McFarlane at the 4th Pan-GEWEX Cloud System Study Meeting, Toulouse, France, June 3, 2008.

Mei D. 2008. "First-Principles Investigation of NO_x Uptake on the y-Al_2O_3 Supported BaO Clusters and Overlayers." Presented by Donghai Mei at the 236th ACS National Meeting, Philadelphia, Pennsylvania, August 19, 2008 (invited).

Mei D. 2007. "Multi-Scale Computational Studies on the Mechanism and the Kinetics of Heterogeneous Catalytic Reactions." Presented by Donghai Mei at the UCSB-PNNL Catalysis Planning Meeting, Santa Barbara, California, December 7, 2007 (invited).

Milbrath BD and Y Zhang. 2008. "Fast Analysis of Potential Scintillators Using Ion Time of Flight." Presented by Brian D. Milbrath at the Northwest Section of American Physical Society, Portland, Oregon, May 16, 2008.

Miracle AL, VL Bailey, SE Baker, AL Bunn, JK Magnuson, and BJM Webb-Robertson. 2008. "Integration of 'Omics Technologies for Characterization of Complex Microbial Ecosystems." Presented by Ann Miracle at the Waste Management Symposium, Phoenix, Arizona, February 26, 2008.

Miracle AL, AL Bunn, JM Brandenberger, and DJ Gaspar. 2008. "Fate and Transport of Titania Nanoparticles in Freshwater Mesocosms." In International Environmental Nanotechnology Conference Proceedings. PNNL-SA-62622, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Mottaz HM, AD Norbeck, JN Adkins, NP Manes, CK Ansong, L Shi, Y Rikihisa, T Kikuchi, S Wong, R Estep, F Heffron, L Pasa-Tolic, and RD Smith. 2008. "Pathogen Proteomics – Making the Pathway Puzzle Pieces Click." Presented by Heather Mottaz at the ABRF 2008 Enabling Technologies in the Life Sciences, Salt Lake City, Utah, February 9, 2008 (invited).

Olsen LC, ME Gross, SN Kundu, and GL Graff. 2008. "Properties of Encapsulated CIGS Cells in 85C/85%RH." Presented by Larry C. Olsen at the 31st IEEE Photovoltaic Specialists Conference, San Diego, California, May 13, 2008 (invited).

Orr G. 2008. "Cellular and Subcellular Interactions with Nanoparticles." Presented by Galya Orr at the National ACS Conference, Philadelphia, Pennsylvania, August 18, 2008.

Orr G, DJ Panther, JL Phillips, BJ Tarasevich, and JG Pounds. 2008. "Nanomaterial with a Specific Set of Properties Can Enter the Cell via Multiple Pathways." Presented by Galya Orr at the Society of Toxicology Annual Meeting, Seattle, Washington, March 16, 2008.

Orr G, DJ Panther, and MG Warner. 2008. "Nanoparticle-Cell Interactions and Intracellular Fate; Roles of Particles Surface Properties." Presented by Galya Orr at the Greener Nano 2008 Conference, Corvallis, Oregon, March 11, 2008 (invited).

Orton CR, JM Schwantes, SA Bryan, TG Levitskaia, DC Duckworth, M Douglas, OT Farmer, CG Fraga, SA Lehn, M Liezers, SM Peper, and R Christensen. 2008. "Advanced Safeguards Technology Demonstration at Pacific Northwest National Laboratory." In Proceedings of the INMM 49th Annual Meeting. PNNL-SA-61320, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Orton CR, JM Schwantes, SA Bryan, TG Levitskaia, DC Duckworth, M Douglas, OT Farmer III, CG Fraga, SA Lehn, M Liezers, SM Peper, and R Christensen. 2008. "Advanced Safeguards Technology Demonstration at Pacific Northwest National Laboratory." Presented by Christopher Orton at the INMM 49th Annual Meeting, Nashville, Tennessee, July 15, 2008.

Padmaperuma AB, PK Koech, X Cai, JL Male, LS Sapochak, and PE Burrows. 2008. "Multi-Functional Materials Containing Carbazole as the Building Block for Improved Charge Balance in Blue OLEDs." Presented by Asanga Padmaperuma at the American Chemical Society Meeting, New Orleans, Louisiana, April 9, 2008.

Peper SM, BK McNamara, MJ O'Hara, and M Douglas. 2008. "A Green Approach to SNF Reprocessing: Are Common Household Reagents the Answer?" Presented by Shane Peper at the 8th International Conference on Facility Operations-Safeguards Interface, Portland, Oregon, April 1, 2008.

Peper SM, BK McNamara, MJ O'Hara, and M Douglas. 2008. "Aqueous Dissolution of Uranium Oxides in Oxidizing Alkaline Media." Presented by Shane Peper at the NRC7 – Seventh International Conference on Nuclear and Radiochemistry, Budapest, Hungary, August 24, 2008.

Qian Y, WI Gustafson Jr, LR Leung, and SJ Ghan. 2008. "Effects of Soot-Induced Snow Albedo Change on Snowpack and Hydrological Cycle in Western U.S. Based on WRF Chemistry and Regional Climate Simulations." Presented by Yun Qian at the 9th WRF Users' Workshop, Boulder, Colorado, June 25, 2008.

Rector DR and ML Stewart. 2008. "Sediment Dynamics Using the Phase Field Method." Presented by David Rector at ECI – Computational Fluid Dynamics in Chemical Reaction Engineering V, Whistler, British Columbia, Canada, June 17, 2008.

Sacksteder CA, JM Jacobs, KM Lee, KM Waters, and DJ Bigelow. 2008. "Identification of RNS/ROS-Modified Proteins as Biomarkers for Chronic Inflammatory Stress in Mouse Lung." Presented by Colette Sacksteder at the Society of Toxicology, Seattle, Washington, March 18, 2008.

Saraf LV, KJ Bunch, MH Engelhard, and PL Gassman. 2008. "Varying Oxygen to Carbon Ratio in Oxyacetylene Flame to Synthesize SiO_2 Nanowires and Amorphous Carbon with sp^3 Hybridization." Presented by Kyle Bunch at the 8th International Conference on Nanotechnology, Arlington, Texas, August 18, 2008.

Scheibe TD, AM Tartakovsky, BJ Palmer, MC Richmond, Y Fang, and BD Wood. 2008. "Pore-Scale Modeling of Reactive and Non-Reactive Transport: Upscaling and Multiscale Hybrid Modeling." Presented by Timothy D. Scheibe at Computational Methods in Water Resources, San Francisco, California, July 6, 2008 (invited).

Sheen DM, DL McMakin, JB Barber, TE Hall, and RH Severtsen. 2008. "Active Imaging at 350 GHz for Security Applications." In Proceedings of the SPIE: Passive Millimeter-Wave Imaging Technology XI, Vol. 6948, p. 69480M. International Society for Optical Engineering, Bellingham, Washington.

Shi L. 2008. "Investigation of Protein-Protein Interactions Related to Salmonella typhimurium Pathogenesis: In Vivo Cross-Linking with Formaldehyde, Tandem Affinity Purification and Mass Spectrometry Identification." Presented by Liang Shi at Joint Genomics: GTL Contractor-Grantee Workshop VI, Bethesda, Maryland, February 11, 2008 (invited).

Shi L, SM Chowdhury, H Yoon, LM Rommereim, AD Norbeck, KJ Auberry, JN Adkins, F Heffron, and RD Smith. 2008. "Investigation of Protein-Protein Interactions Related to Salmonella typhimurium Pathogenesis: In Vivo Cross-Linking with Formaldehyde, Tandem Affinity Purification and Mass Spectrometry Identification." Presented by Liang Shi at the ASM Annual General Meeting, Boston, Massachusetts, June 3, 2008.

Song C, RA Zaveri, ML Alexander, JA Thornton, S Madronich, JV Ortega, A Zelenyuk, XY Yu, A Laskin, and AD Maughan. 2008. "Effect of Pre-Existing Primary Organic Aerosols on Secondary Organic Aerosol Formation Yields." Presented by Rahul A. Zaveri at the Seminar at the National Oceanic and Atmospheric Administration, Boulder, Colorado, July 30, 2008 (invited).

Straub TM, RA Bartholomew, A Dohnalkova, NB Valentine, CJ Bruckner-Lea, CP Gerba, P Orosz Coughlan, B Mayer, MA Abbaszadegan, D Fernandez, E Richter, M Herbst-Kralovetz, CA Nickerson, D Kingsley, J Woods, K Calci, and J Hewitt. 2008. "From Single to Multiple Laboratories: Norovirus Cell Culture." Presented by Tim Straub at the International Professorship at ESR, New Zealand, February 28, 2008 (invited).

Straub TM, RA Bartholomew, DS Wunschel, JH Wahl, N Beagley, JZ Hu, Y Lin, and SM Varnum. 2008. "Preliminary Data on Integrated 'Omics' Approaches for Biomarkers of Human Infectious Diseases." Presented by Tim Straub at the International Professorship at ESR, New Zealand, February 28, 2008 (invited).

Sundaram SK. 2007. "Materials and Sensors for Gasification." Presented by SK Sundaram at MIT Materials Science and Engineering, Cambridge, Massachusetts, November 20, 2007 (invited).

Sundaram SK, BJ Riley, JV Ryan, JV Crum, HA Qiao, and NC Anheier, Jr. 2008. "THz Spectroscopy of Photomodified Chalcogenide Glasses." Presented by Joseph Ryan at the ACerS Glass and Optical Materials Division Meeting, Tucson, Arizona, May 19, 2008.

Tang K, ES Baker, EA Livesay, DJ Orton, B Danielson, III, DC Prior, AM Mayampurath, RT Kelly, JS Page, and RD Smith. 2008. "A High Throughput LC-IMS-MS Platform for Sensitive and Quantitative Proteomics Analysis." Presented by Keqi Tang at the 56th ASMS Conference on Mass Spectrometry and Allied Topics, Denver, Colorado, June 2, 2008.

Taylor RC. 2008. "Reconstruction of Biological Networks Using the Software Environment for Biological Network Inference (SEBINI)." Presented by Ronald C. Taylor at the University of North Carolina at Charlotte, Charlotte, North Carolina, July 26, 2008 (invited).

Taylor RC. 2008. "Reconstruction of Biological Networks Using the Software Environment for Biological Network Inference (SEBINI)." Presented by Ron Taylor at the Bioinformatics and Computational Biology Department at the University of Texas, Houston, Texas, September 4, 2008.

Teeguarden JG. 2007. "Advancing Hazard Assessment and Dosimetry for Nanomaterial Risk Assessment." Presented by Justin Teeguarden at the California EPA – Department of Toxic Substance/Nanotechnology Symposium II, Sacramento, California, December 12, 2007 (invited).

Teeguarden JG. 2007. "Advancing Hazard Assessment and Dosimetry for Nanomaterial Risk Assessment." Presented by Justin Teeguarden at the DTSC Nanotechnology Symposium II: Potential Hazards of Nanoparticles in the Environment, Sacramento, California, October 3, 2007 (invited).

Teeguarden JG. 2008. "Nanomaterial Dosimetry and Risk Assessment." Presented by Justin Teeguarden at the Society of Toxicology, Seattle, Washington, March 16, 2008.

Thrall BD, KM Waters, LM Masiello, BJ Tarasevich, and RC Zangar. 2007. "Analysis of Size-Dependent Cellular Responses to Silica Nanoparticles from Integrated Genomic and Proteomic Data." Presented by Brian Thrall at the Society of Toxicology, Seattle, Washington, March 18, 2007.

Towne SA, VV Viswanathan, PC Rieke, and JD Holbery. 2007. "Fabrication of Polymer Electrolyte Membrane Fuel Cell MEA's Utilizing Inkjet Print Technology." Presented by Silas Towne at the MRS Spring Conference, San Francisco, California, April 12, 2007 (invited).

Trease HE, F Dan, RM Farber, and ST Elbert. 2008. "Using Transaction Based Parallel Computing to Solve Graph Problems Associated with High-Throughput Video Surveillance Applications." In TeraGrid '08. PNNL-SA-60172, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Wahl JH and CJ Bruckner-Lea. 2008. "A Human Breath and Condensate Model: Exposure and Signature Discovery Using 3-Dimensional Human Tissue Cultures for Threat Characterization." Presented by Jon Wahl at the DARPA Human Breath Analysis Workshop, Livermore, California, February 6, 2008 (invited).

Waters KM. 2008. "Computational Challenges for the Integration of Genomics and Proteomics Data in Determining Toxicity Pathways." Presented by Katrina Waters at the National Institute on Aging Bio-Signatures Workshop, Bethesda, Maryland, May 2, 2008.

Waters KM, NJ Karin, BJM Webb-Robertson, RC Zangar, JG Pounds, and BD Thrall. 2008. "Integration of Microarray and Proteomic Data Reveals Nanoparticle-Specific Inflammatory Markers in Mouse Macrophage Cells." Presented by Katrina Waters at the MicroNano Breakthrough Conference 2008, Vancouver, Washington, September 9, 2008.

Webb-Robertson BJM. 2008. "Models for A Priori Identification of Proteotypic Mass Spectrometry Peptides and Proteins." Presented by Bobbie-Jo Webb-Robertson at the Third Annual BioProcess International Analytical and Quality Summit, Cambridge, Maryland, June 4, 2008 (invited).

Weber TJ, SK Sundaram, JG Teeguarden, BJ Riley, LS Fifield, JM Jacobs, S Addleman, GA Kaysen, and BM Moudgil. 2008. “Adsorbed Proteins Influence the Biological Activity and Molecular Targeting of Nanomaterials.” Presented by Tom Weber at the Society of Toxicology, Seattle, Washington, March 18, 2008.

Wigmosta MS. 2008. “Advanced Streamflow Forecasting.” Presented by Mark Wigmosta at the Okanogan RC&D Council Meeting, Chelan, Washington, March 12, 2008 (invited).

Williford RE and CE Beyer. 2008. “Thermal Conductivity Model for MO_X with <10% Actinides.” Presented by Carl Beyers at the American Nuclear Society (ANS) Topical Meeting, Anaheim, California, June 9, 2008 (invited).

Williford RRE, VV Vishwanathan, and J Zhang. 2008. “Effects of Entropy Changes in Anode and Cathode on Thermodynamic Behavior of Li Ion Batteries.” Presented by Jason Zhang at the 14th International Meeting on Lithium Batteries, Tianjin, China, June 23, 2008 (invited).

Williford RRE, VV Vishwanathan, and J Zhang. 2008. “Effects of Entropy Changes in Anode and Cathode on Thermodynamic Behavior of Li Ion Batteries.” In Journal of Power Sources. PNNL-SA-61086, Pacific Northwest National Laboratory, Richland, Washington. [Unpublished]

Wynne AS and I Gorton. 2008. “A Flexible, High Performance Service-Oriented Architecture for Detecting Cyber Attacks.” Presented by Adam Wynne at Hawaii International Conference on System Sciences (HICSS), Waikoloa Village, Hawaii, January 7, 2008.

Xie YL, F Gao, R Devanathan, AJ Peurrung, and WJ Weber. 2008. “Applications of Monte Carlo Method to Simulate X-ray Interaction in Xe.” In IEEE-9th International Conference on Inorganic Scintillators and Applications, p. 172. IEEE SCINT 2007, Winston-Salem, North Carolina.

Young J, SE Thompson, AJ Brothers, PD Whitney, GA Coles, CL Henderson, and BL Hoopes. 2008. “The Use of Dynamic Stochastic Social Behavior Models to Produce Likelihood Functions for Risk Modeling of Proliferation and Terrorist Attacks.” Presented by Jonathan Young at PSAM9, Hong Kong, China, May 20, 2008.

Zentner MD, GA Coles, and I Therios. 2008. “A Qualitative Assessment of Diversion Scenarios for a Example Sodium Fast Reactor Using the Gen Iv Pr&Pp Methodology.” In International Nuclear Materials Management Conference, July 2008.

Zhang Y, BD Milbrath, and WJ Weber. 2008. “Ion Technique for Screening Gamma Detector Candidate Materials.” Presented by Yanwen Zhang at the 2008 Symposium on Radiation Measurements and Applications, Berkeley, California, June 2, 2008.

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NATIONAL LABORATORY

U.S. DEPARTMENT OF
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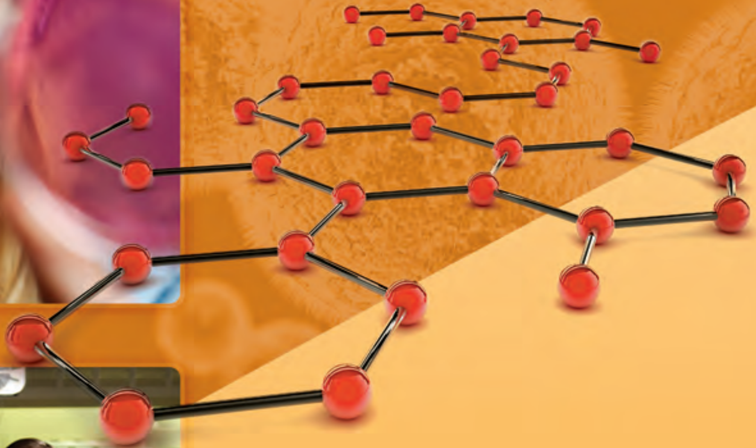
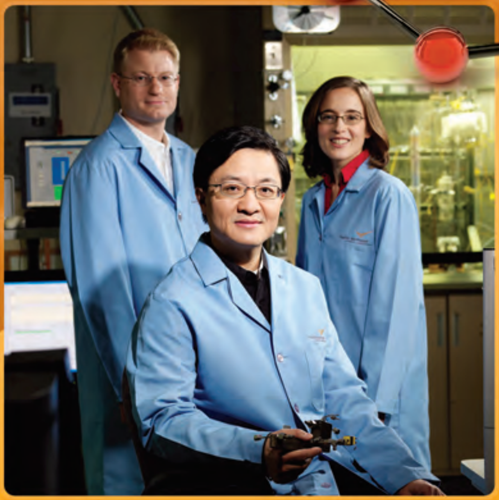
ANNUAL REPORT 2008

Laboratory Directed Research & Development





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Pacific Northwest National Laboratory seeks to continually replenish its inventory of ideas, which have the potential to address major national needs.

The principal goals of Laboratory Directed Research and Development are to encourage the advancement of basic science and fundamental research at the Laboratory and develop new technical capabilities from which future research and development programs will grow.